ELECTRO--CHEMICAL AGGREGATE--ASPHALT RESEARCH PROJECT

by
Montana Highway Department
Materials Division

<u>Final Report</u>
Study of the Electro--Chemical Reactions in
an Aggregate--Asphalt System
Research Project HPR 1(2): Item R-8

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INTRODUCTION

Nature and History

This project consists of a number of diversified studies relating to the nature of asphalt adhesion. The basic intent was to shed light onto the problems of stripping and ravelling, and to provide means to mitigate them. The Materials Laboratory has done sporadic work in this area for over forty years as time and personnel have permitted, and this study, in cooperation with the Bureau of Public Roads, represents the most recent endeavor.

Earlier work at the Materials Laboratory centered around obtaining an acceptable stripping test. The old A.S.T.M. procedure leaves a great deal to be desired in that while it perhaps isolates a very bad asphalt or aggregate, it fails to provide any information concerning the good ones. An improved test was devised and has been in use now for some time. It has been reported in the highway literature and is discussed in detail in connection with the action of adhesive agents. Its development brought forth a semi-quantitative way of classifying aggregates according to adhesion ability and also provides a means of determining the quality or presence of an adhesive agent.

The drastic differences between various bituminous asphalt and aggregate materials in relation to adhesion raises fundamental questions concerning the adhesive mechanism and factors which influence it. It is natural then to try to proceed in a more fundamental direction. This was first attempted a number of years ago in a cooperative project with the Montana School of Mines in measuring the electrokinetic or zeta potential associated with streaming on mineral surfaces. It was hoped that the potentials would provide a satisfactory quantitative way of evaluating

mineral surfaces according to adhesion ability and might also explain the stripping phenomena. As of the present, such studies have not provided conclusive data.

In studying adhesion, concern is with three things: asphalt, aggregates, and interactions. Consequently the project is divided into three phases. The asphalt studies represent the bulk of the effort. In the following report, the studies will be grouped accordingly, rather than by the chronological order of their performance. Occasionally, there are deviations from the original purpose in order to exploit available instrumentation and to open new areas of inquiry.

Viewpoint

Since the research group consisted of two chemists, one physicist, and several technicians, the research methods and thinking reflect that of the pure scientist rather than that of the engineer. There are several differences which should be mentioned. Engineering thinking tends to be inductive and to rely heavily on accumulated field experience. Engineering measurements seek to duplicate a desirable field property in a material. A particular test gains validity by virtue of continued successful use. A particular property is defined only by the test used to measure it; e.g., penetration can be defined only in terms of the penetration test. The physical scientist does not try to duplicate a field condition but very carefully controls a system so that he can measure a quantity having a precise mathematical definition. Every system possesses a definite number of such quantities which can be called independent parameters. Once these independent parameters are known, any other physical property or behavior can be calculated, including those of importance to the engineer. The parameters commonly chosen are the thermodynamic constants and the kinematic parameters,

e.g., coefficient of expansion, bulk moduli, heat capacities, diffusion coefficients, viscosity, elasticity, etc. Where the variables can be isolated, the number of measurements needed is relatively small. It is precisely the fact that variables are not isolated that requires the engineer to obtain large amounts of data and then do statistical reductions before he can be sure of a particular test. It is of interest to note that those tests which survive this process are most likely to be simple functions of the parameters indicated above, although the exact relationships involved are usually unknown.

In physico-chemical studies it is possible to proceed in either of two ways. The first assumes a macroscopic viewpoint and then describes the system of interest in terms of a set of thermodynamic parameters as indicated above. No mention need be made as to the exact composition or the detailed structure of the system. The second method assumes a microscopic viewpoint and is concerned with the precise atomic nature of the system. The latter viewpoint is termed quantum-mechanical and is concerned with the nature of chemical bonding, molecular architecture, crystal defects, etc. It is immediately clear that any hope at a detailed knowledge of systems as complicated as asphalt or aggregates is wishful thinking. No two samples of the material will be identical. Since, however, the properties which are of interest in an engineering world are gross properties, the first mode is entirely adequate.

In the case of asphalt it has been possible to obtain a qualitative connection between physical properties and the more gross chemical features. Infra-red analysis has proved to be of use in this connection but the resulting spectra are difficult to interpret and correlations are of a subtle nature.

Terminology

The terms adhesion and cohesion are often used. Cohesion refers to

the ability of a homogeneous material to stick together. Adhesion refers to the ability of one material to stick to another. The ratio of adhesive to cohesive forces determines the stickiness or tackiness of a material. If the adhesive forces greatly exceed the cohesive forces, the one material is said to wet the other. When both adhesive and cohesive forces are large and nearly equal, the material makes a good cement or glue.

The use of asphalt as an adhesive for stone depends on both adhesion and cohesion. The ravelling of clean rock from an asphalt pavement indicates that the cohesive forces are larger than the adhesive forces while the ravelling of an asphalt-coated rock indicates the converse. Since the mechanism for adhesion and cohesion may be slightly different, improvements may be possible in both directions.

PART I-A
ASPHALT STUDIES

Hydrogen Bonding

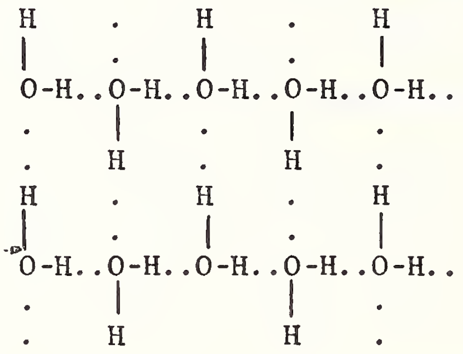
The study of the relationship of composition of bituminous materials to adhesive properties has been receiving increasing attention. The role that the adhesion promoting components play is not clear at the present time. Various theories have been introduced to explain their action, but these are unsatisfactory either from an experimental viewpoint or in that they ignore a good deal of twentieth century science. One purpose of this paper is to propose a theory for asphalt adhesion that is satisfactory with respect to these criteria.

It is expected that hydrogen bonding should play an important role in determining the physical properties of asphalt. A series of measurements were made to determine the internal bonding energy in asphalt, and this value has been found to correspond to weak hydrogen bonding. The temperature dependence of viscosity, deielectric constant and conductivity can be related to the internal bonding energy of the asphalt by means of appropriate equations. These studies are offered as evidence of the validity of a hydrogen bonding concept. The phenomena of stripping and ravelling as well as the action of the amine agents can be explained in terms of the hydrogen bonding influence. It also serves as a useful reference point in the interpretation of I.R. spectra as will be indicated later.

The Nature of Hydrogen Bonding

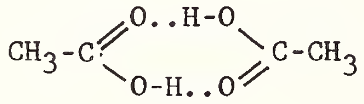
The reader is referred to the bibliography for a detailed discussion of hydrogen bonding. An elementary discussion is included here for heuristic purposes.

Hydrogen bonding is a process whereby certain simple molecules containing hydrogen can cluster together to form long chains or networks. The most important example of this occurs in water. In the liquid and solid state, the following structure exists.



This particular link indicated by the dots is called a hydrogen bond. In the form of steam, water exists as a collection of single molecules. Such a linking or association occurs in all substances where hydrogen is connected to a more electronegative atom such as oxygen, chlorine, sulfur or nitrogen. Such bonding can also occur in hydrocarbon mixtures containing these elements.

Another important example is acetic acid. This exists in the form of a dimer.



Organic acids form strong hydrogen bonds. The hydrogen bond here is about twice as strong as that in ice.

Hydrogen bond strengths are tabulated according to the energy involved in their formation. A brief list is indicated on the following page.

Table I

Hydrogen Bond Energy Values*

Bond	Energy	Substance
F-H-F	6.7 kcal	H_6F_6
O-H...O	4.5	Ice $(H_2O)_2$
O-H...O	8.2	$(CH_3COOH)_2$
O-H...O	7.06	$(HCOOH)_2$
C-H...N	3.28	$(HCN)_2$
C-H...N	4.36	$(HCN)_3$
N-H...N	1.3	(NH_3)

The hydrogen bonding energy is closely related to the heat of vaporization of a material. The latter is only slightly greater than the former for most liquids. The hydrogen bond energy values refer, however, to the specific bond indicated, rather than to the sum total of all the interactions in the system. The energies are on a molar scale, i.e., the energy in Kcal. needed to break 6.02×10^{23} such bonds.

For comparison purposes, the following miscellaneous bond energies are included here:*

Table II

Miscellaneous Bond Energy Values*

Bond	Energy
H-H	103 kcal/mole
C-C	58 kcal/mole
C-H	87.3 kcal/mole
N-H	83.1 kcal
C-N	48.6 kcal
C-O	70
C-S	54
Si-O	89.3
H-Cl	102.7

*From Pauling, The Nature of the Chemical Bond.

Hydrogen bonding is relatively independent of the nature of the hydrocarbon, but the presence of oxygen, sulfur or unsaturates should be important in that these effect the extent and type of hydrogen bonding. The extent of hydrogen bonding can be expected to determine the rheological properties of asphalt. Hydrogen bonding at the terminal atoms increases effective chain length and results in a more rubber-like material. Bonding between side chains or cross linking, as it is called, results in a more brittle material. As the temperature is raised, these bonds are broken by thermal motion and the material resembles a conventional liquid.

As a rule, atoms having the strongest electronegativity tend to form the strongest hydrogen bonds. A short bond distance also favors a strong bond. This distance depends on the geometry of the respective molecules.

(1) Viscous Flow Activation Energies

The Eyring transport theory allows calculation of the free energy of activation for viscous flow in liquids. This model can be applied to asphalt and provides a means of obtaining the average bond energy value.

The reader is referred to Herschfelder et. al. (1) for a more complete discussion of this theory and its limitations. The model assumes that a lattice exists within the liquid. The production of a hole or lattice vacancy requires the expenditure of an amount of energy G equal to the total bonding energy of any one molecule with all of its nearest neighbors. At any given temperature the number of holes is proportional to a Boltzmann factor exp $-\Delta G/kT$. Fluid flow is visualized as taking part via these holes. When a force is applied to the system, the potential energy surface associated with a hole is distorted, and a preferential movement into holes in the direction of the force results. The extent of the motion can be calculated and the following formula for the viscosity coefficient derived.

(a) $$\frac{F\delta}{2aK'_0 \sinh(aF/2n\delta kT)} = \eta$$

F is the external force, δ is the distance between adjacent slip planes, a is the distance between lattice sites, n is the number of molecules per unit volume, k is the Boltzmann constant, T is the absolute temperature and K'_0 is the transmission coefficient in the absence of applied force.

If the forces are small, then the flow becomes Newtonian, and a Taylor expansion of (1) and substitution of K'_0 yields:

(b) $$\eta = \left(\frac{\delta}{a}\right)^2 \frac{nKT}{K'_0} = \left(\frac{\delta}{a}\right)^2 nhe^{\Delta G/RT}$$

A plot of log η versus 1/t has a slope of $\Delta G/R$. ΔG is the Gibbs free energy of activation for the flow and represents the average bond energy between a molecule and its nearest neighbors.

(c) $$\text{Log}\ \eta = \text{Log}\ \left(\frac{\delta}{a}\right)^2 nh + \frac{\Delta G}{RT}$$

Plate (1) shows a plot of this for Diamond SC-250 asphalt. A value of 16.4 Kcal/Mole is obtained for ΔG for this asphalt.

The viscosity was measured using a Saybolt viscometer and the appropriate kinematic conversion factor. The experimental data is fairly rough, but the value of ΔG should be quite accurate due to the logarithmic factor.

Due to lack of appropriate equipment, no attempt was made to obtain complete curves for different types of asphalts.

Calculations of ΔG were made on the basis of kinematic viscosity values obtained from the literature. Since the viscosity values are given

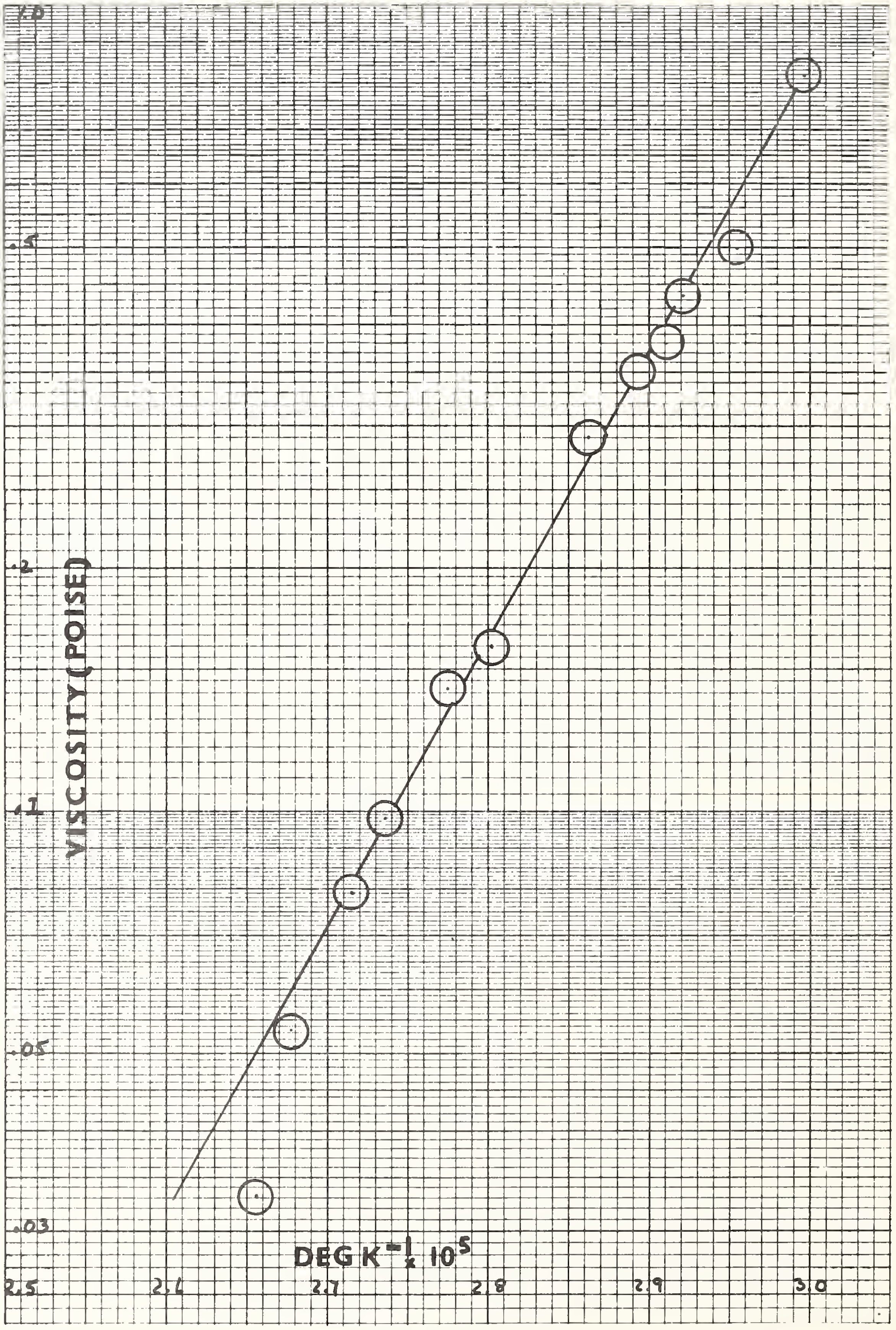


PLATE I

at only two or three temperatures, these ΔG values are indicative rather than conclusive. The logarithmic factor will smooth out any large deviations however. Table III gives calculated values for different types of penetration asphalts while Table IV gives the same values for cutbacks. The data used was taken from the Report of Kinematic Viscosity Measurements; Missouri State Highway Department (1963).

In the past, logarithmic viscosities of asphalt have been plotted against Fahrenheit temperature. Such graphs have interpolative value, but lack theoretical significance. The fact that the log η is a near linear function of the Fahrenheit temperature does not imply that it cannot be a near linear function of the reciprocal of the absolute temperature over some range. If the viscosity is a function of the temperature, then a Taylor expansion in T will be linear over a range of low temperatures, while the same expansion in terms of 1/T will be linear for high temperatures. The relative size of the non-linear intermediate region will depend on the precise nature of the function. If the function is near linear, then the range will be small.

An equation expressing an identical temperature dependence to (2) can be derived from the diffusion equation. For details, the reader is referred to Frenkel, (3).

The very close precision of the ΔG values for the different asphalts indicates that the internal interactions in asphalt are more or less independent of the crude used or the particular refining process. ΔG represents the bond energy on a molar scale between any molecule and its nearest neighbors. If six nearest neighbors are assumed, then each bond has a value of about 2.7 Kcal/Mole which indicates a weak hydrogen bond.

Table III*

Data on Penetration Asphalt Grade 70-85

Refinery	300°F Viscosity** (Centistokes)	275° Viscosity** (Centistokes)	(Kcal./Mole)
J	205.6	392.1	15.93
F	167.1	317.7	15.91
P	246.9	466.5	15.69
R	270.9	507.0	15.52
E	267.0	514.3	16.17
N	184.0	350.0	16.43
L	143.7	269.0	15.47
I	181.1	339.8	15.52
S	243.6	456.0	15.47
M	242.4	460.1	15.81

*Taken from <u>Report of Kinematic Viscosity Measurements</u>, Missouri State Highway Department (1963) pp. 20-24 appendix.

**These are average values of several measurements.

Table IV

Data on Cutback Asphalts*

Refinery	Type	Viscosity (cs) 122°	Viscosity (cs) 180°	
H	MC-0	64.4	42.5**	8.838
O	MC-0	76.5	51.3**	8.500
L	MC-1	274.1	54.4	11.46
A	MC-2	573.0	100.8	12.31
B	MC-2	644.9	113.6	12.31
A	MC-3	1433.0	193.0	14.21
C	MC-3	1917	237.5	14.80
B	MC-4	4500	449.3	16.33
H	MC-4	3991	400.0	16.30
G	MC-5	19643	1132	20.02
I	MC-5	15300	967	19.57
B	RC-5	12952	935	18.63
B	RC-4	3481	372.7	15.84
I	RC-4	3911	379.6	16.53
H	RC-3	1762	216.2	14.87
B	RC-3	1420	198.3	13.95
B	RC-1	246.1	56.2	10.47
B	RC-0	74.3	49.3**	8.725
I	SC-4	2181	233.7	15.83
I	SC-3	1179	144.4	14.88
H	SC-2	420	59.1	13.90
I	SC-1	230	45.2	11.53

*Taken from Report of Kinematic Viscosity Measurements, Missouri State Highway Department (1963) pp. 8-17 appendix.

**These viscosities are at 140°F instead of 180°.

No attempt has been made to correlate the ΔG values with the penetration values for the asphalts, but we observe a significant trend in that the heavier asphalts show much higher bonding energies.

This model predicts a non-Newtonian flow property for asphalt. This property could easily be checked against equation (1). The only unknown parameter is the lattice spacing which could then be calculated. In the case of non-Newtonian fluids, two different viscosity coefficients exist at a particular temperature (9) depending on the applied force. This may account for the lack of correlation encountered in measuring asphalt viscosities by different methods. This difference, however, does not alter the validity of our calculation as the difference makes its appearance in the intercept, not the slope of the viscosity curves.

Part II The Dielectric Properties of the SC-250 Asphalt

Substances with extensive hydrogen bonding show high dielectric constants. The association process increases the effective dipole moment, and hence the dielectric constant.

The dielectric constant of asphalt has been studied as a function of temperature. Plate (2) shows a schematic diagram of the experimental setup used. An SC-250 was again used so that a correlation of results would be possible and also because of its low viscosity. Plate (3) shows a graph of the dielectric constant versus temperature for several successive measurements.

Initially the asphalt was heated to about 70°C, where it becomes quite mobile. The capacitor assembly was immersed into the hot asphalt and moved about to remove any air trapped between the plates. The assembly was allowed

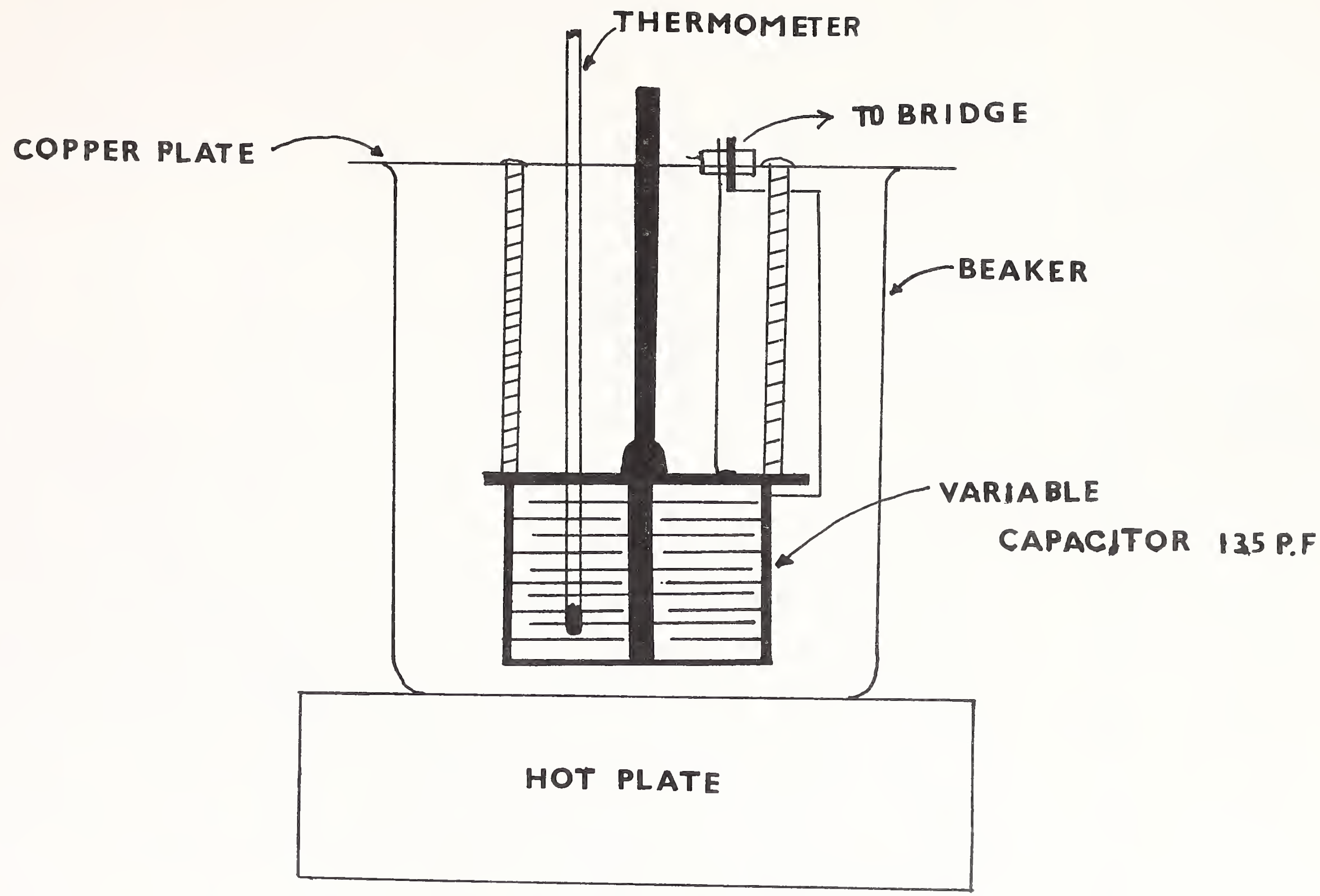


PLATE 2 EXPERIMENTAL SETUP

to cool and then the temperature was elevated using a hot plate. An Electro Scientific Industries 250 D.A. impedance bridge was used to observe the capacitance as the temperature was raised. Observations were made at one or two degree intervals and were also made while the system cooled. The curves obtained by cooling are more significant than those recorded during heating since some temperature gradients exist within the system at this time.

Heating of new samples tended to yield reproducible data while repeated heating of a single sample yielded displaced curves. These displacements are related to the small amounts of water released by heating. During atmospheric exposure, water was reabsorbed to replenish part of that lost. Several conclusions can be drawn from this. Since temperatures as high as 200°C were attained in the heating in certain cases without drastic changes in the samples, the water must be present in a tightly bonded state. The tendency of the asphalt to reclaim water from the atmosphere indicates that there is most likely a certain "equilibrium" concentration of water in the asphalt.

Conductivity similarly decreased upon frequent heating indicating that the material lost must be both polar and ionic. The loss of purely organic constituents would not be expected to influence these properties in this direction. A loss of volatiles should result in a more concentrated solution with a higher conductance, but the opposite was observed. An increase in viscosity would result in a decrease in conductance, but an increase of sufficient magnitude was not observed.

Some interesting facts are evident from the graph of dielectric constant versus temperature (Plate 3). At temperatures below about 65°C there is no free molecular rotation. The dielectric constant is due entirely to

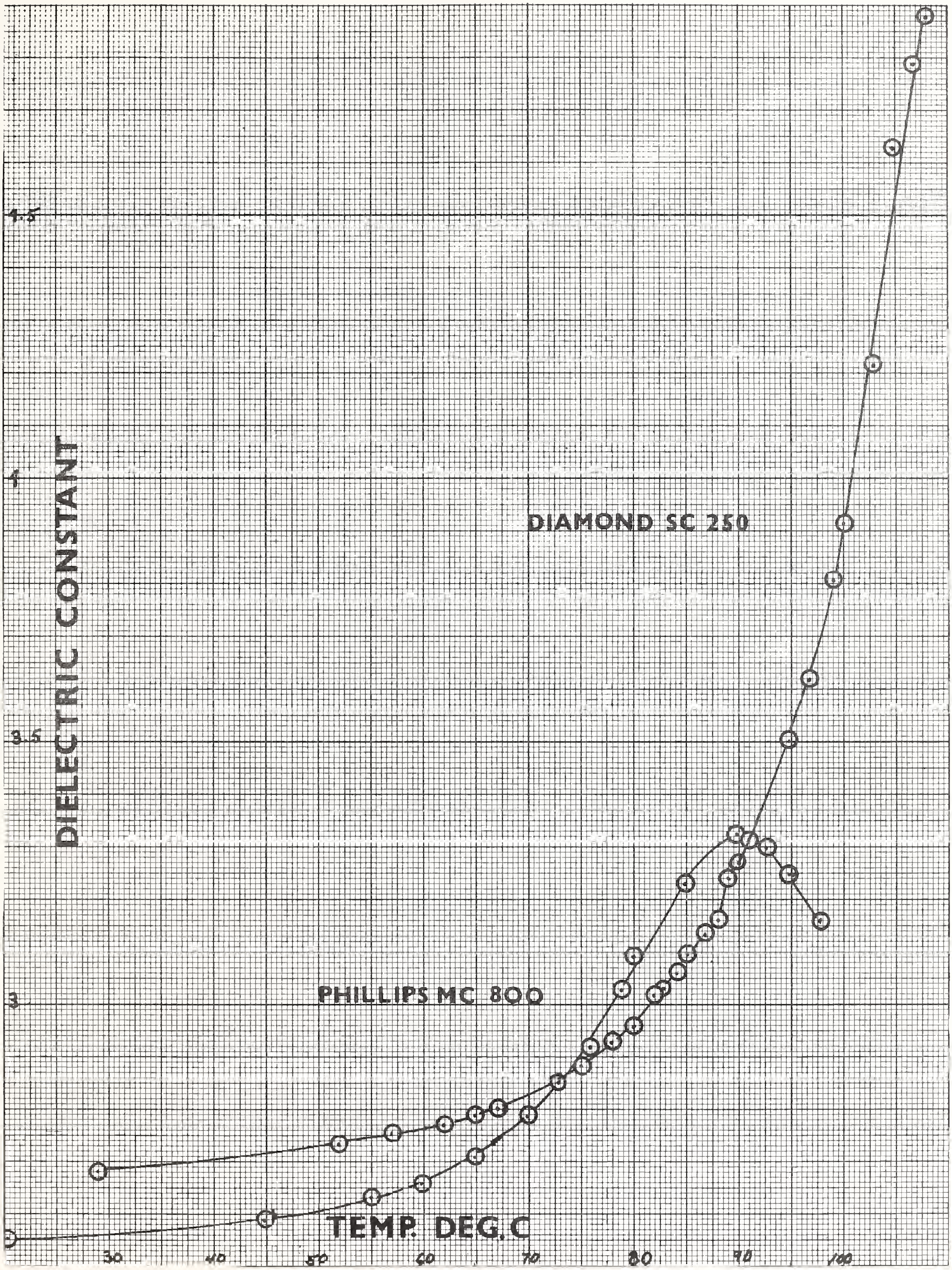

4.5
4
3.5
3
DIELECTRIC CONSTANT
DIAMOND SC 250
PHILLIPS MC 800
TEMP. DEG. C
30
40
50
60
70
80
90
100

PLATE 3

electronic polarizations and compares with the value of non-polar hydrocarbons. At temperatures greater than this, small rotations of polar groups contribute to the dielectric constant. It is generally known that deviations from the Eyring model are due principally to rotational effects which tend to lower the flow activation energy. The dielectric studies then provide estimates of where deviations in the viscosity behavior should occur.

A complete theoretical analysis of the system is not possible due to its unknown composition, but a very general treatment can be given. The temperature dependence of the dielectric constant can be attributed to three effects.

(1) <u>Langevin Dependence</u>

The component of the average dipole moment in the field direction gives rise to a polarization having a general dependence of the form:

$$P \sim \int_0^{\pi/2} e^{-\mu \cos \theta / kT} \mu \cos \theta \, d\theta \tag{4}$$

Since the field interaction energy $E \ \cos \Theta$ is small, this will not cause drastic changes in the dielectric constant over a temperature range as small as 50°C. This term yields a contribution which decreases with increasing temperature.

$$D \sim \mu / 3RT \tag{5}$$

We can neglect this in our calculations.

(2) <u>Viscosity Dependence</u>

As the material is heated, the viscosity decreases and this results in a greater degree of rotation for polar groups. If the mean dipole moment is assumed constant, then the dielectric constant should be inversely proportional to the viscosity. We can alternately assume a free energy of activation for rotational motion, i.e., before a molecule is

free to rotate, it must acquire an energy G'. This energy can be identified with that bonding energy which tends to hold the polar molecule rigid. The number free to rotate at any given temperature will then be given by the Boltzmann factor $N_o \exp - G'/kT$. N_o is the concentration of polar groups in the system.

(3) Association Dependence

If the mean dipole moment of the system is temperature dependent, then we should expect some interesting effects. There are two possible cases. (a) Associated dipoles in the system rotate as single molecules. As the temperature is raised we have dissociative equilibria with the mean dipole moment decreasing in accordance with the dissociation. Since such an association involves a greater interaction energy than between heterogeneous groups, this effect should show up at relatively high temperatures. (b) High temperatures promote ionization of certain constituents. These ions then attach themselves to non-polar molecules which become polar. Due to the hydrocarbon nature of the asphalt this can be assumed to be small.

Plates (4) and (5) show a plot of the dielectric constant versus viscosity and a plot of log $(D-D_o)$ versus $1/T$. D_o is the polarization contribution to the dielectric constant, and is not temperature dependent.

Assume

(6)
$$D = C e^{-\Delta G'/RT} + D_o$$

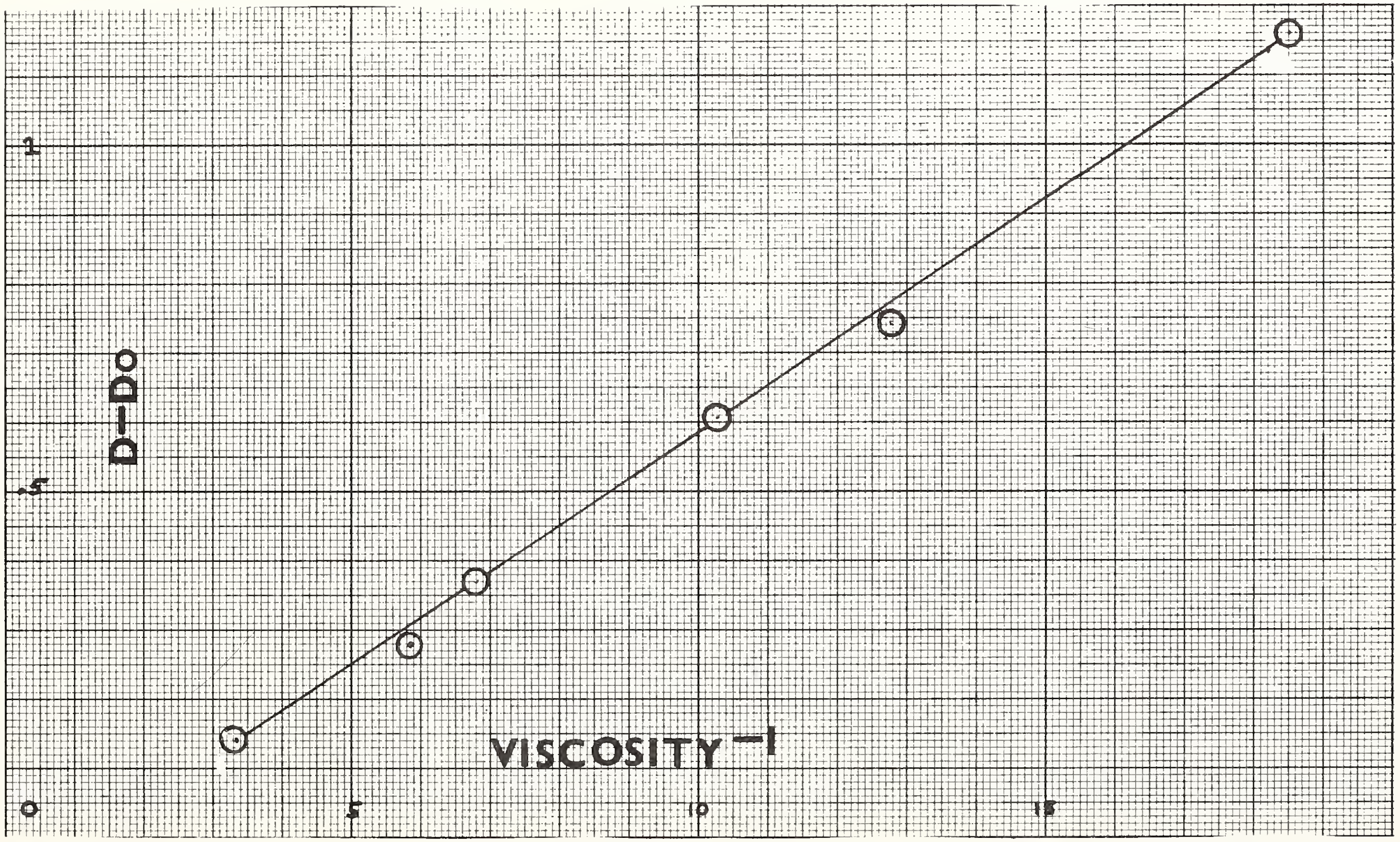
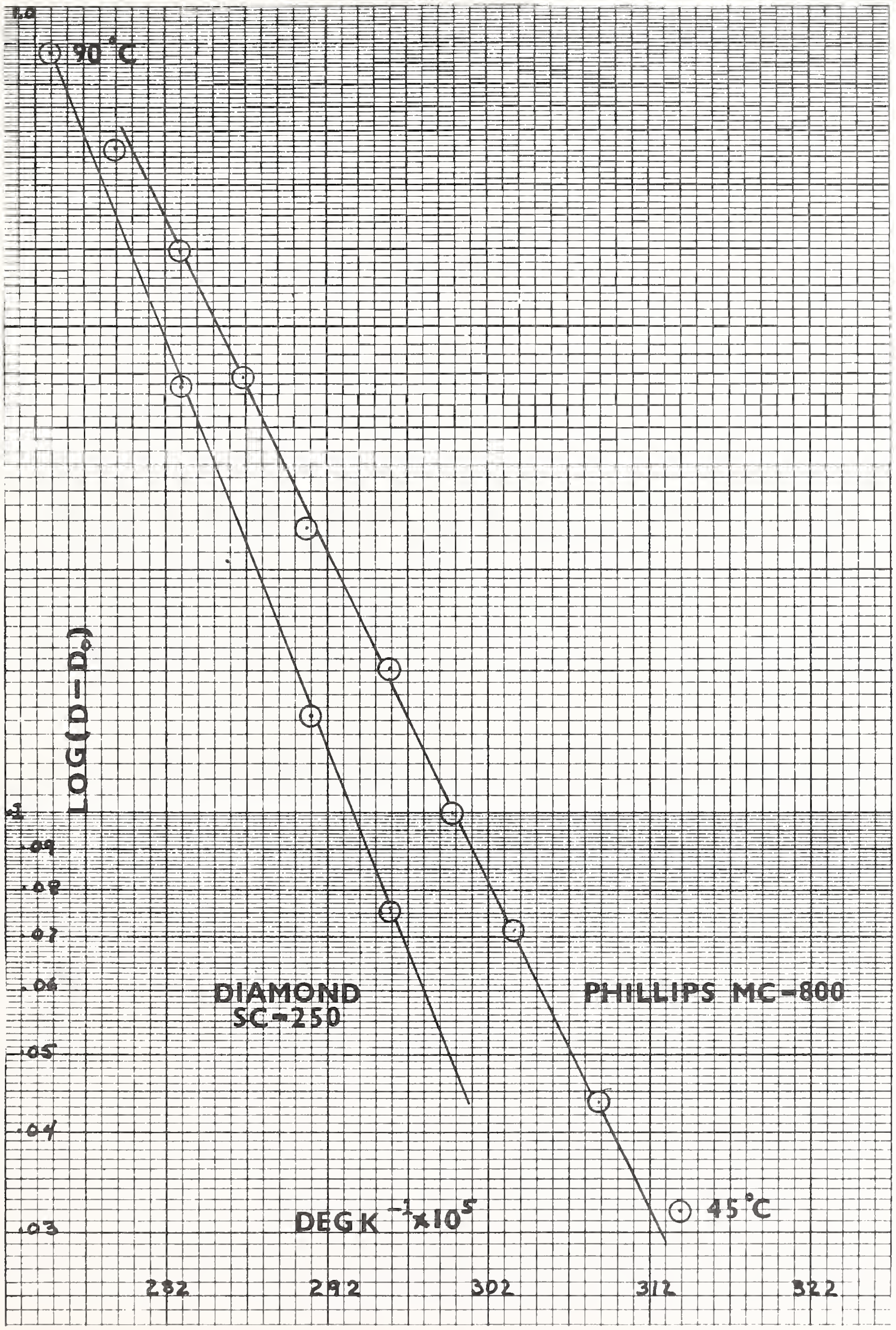


PLATE 4 DIELECTRIC VS VISCOSITY



90°C
LOG(D − D₀)
1.0
.1
.09
.08
.07
.06
.05
.04
.03
DIAMOND
SC-250
PHILLIPS MC-800
45°C
DEG K⁻¹ × 10⁵
282
292
302
312
322

PLATE 5

Picking two points on the line;

$$\text{(7)} \qquad \text{Log} \; \frac{(D_1 - D_o)}{(D_2 - D_o)} = \frac{\Delta G'}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

and

$$\text{(8)} \qquad \Delta G' = \left(R \; \text{Log} \; \frac{D_1'}{D_2'} \right) \left(\frac{T_1 T_2}{T_2 - T_1} \right)$$

Points 83 and 103 yield a value of 27.3 Kcal/Mole.

The viscosity effects are evidently dominant in this sample. The higher activation energy is due to the fact that we are dealing with the average polar molecule which bonds more strongly than the non-polar constituents. The bond energy for the polar groups therefore is of the order of 4.6 Kcal/Mole which compares with the hydrogen bonding energy of water in ice (4.5 Kcal/Mole).

Part III The Conductance of Asphalt as a Function of Temperature

Asphalt has been observed to conduct an electric current, the D.C. specific conductance being on the order of 6×10^{-5} mhos/cm. The temperature dependence of the conductance is found to be due to changes in the viscosity and dielectric constant only, which indicates that the water exists within the asphalt in a completely ionized state, or at least that un-ionized water is bonded and is not free to ionize. The conductance varies as the asphalt gains and loses water from the atmosphere.

The Cardwell 137.5 mmf variable air capacitor was used as a conductivity cell. This corresponds to a cell constant of 6.44×10^{-4} cm^{-1}. The same procedure and setup was used here as in the dielectric study. All

measurements were made using a direct current. The cell resistance was observed at constant temperature over a period of several hours to check against possible electrolysis of the aluminum plates in the capacitor. No change in the resistance was observed.

Plates (6) and (7) show the conductance as a function of temperature.

Theory of Conduction

The current flowing in the system is given by:

$$I = \sum_i P_i q_i |V_i| A \tag{9}$$

Where P_i is the density of the ith conducting species, q_i is its charge and $/V_i/$ is its speed. A is the plate area of the cell.

Assuming Stokes' law to hold for the moving ions, the terminal speed will be given by

$$|V_i| = \Phi q_i / 6\pi D r_i \eta L \tag{10}$$

Where Φ is the potential across the cell, L is the distance between plates, D is the dielectric constant of the media, and r is the mean ionic radius.

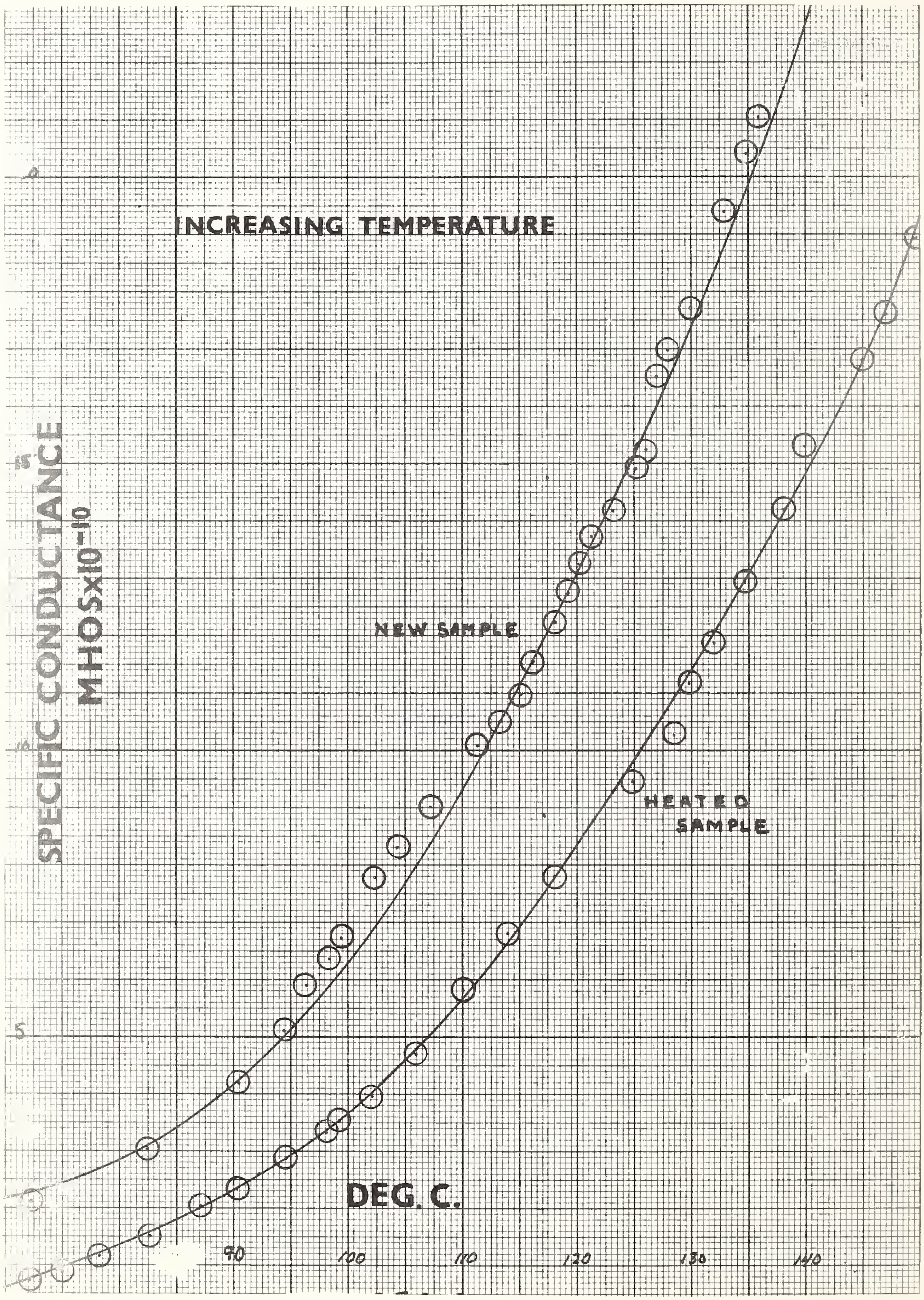
For small currents, Ohm's law holds and

$$I = \frac{A}{L} \sigma \Phi \tag{11}$$

σ being the specific conductance.

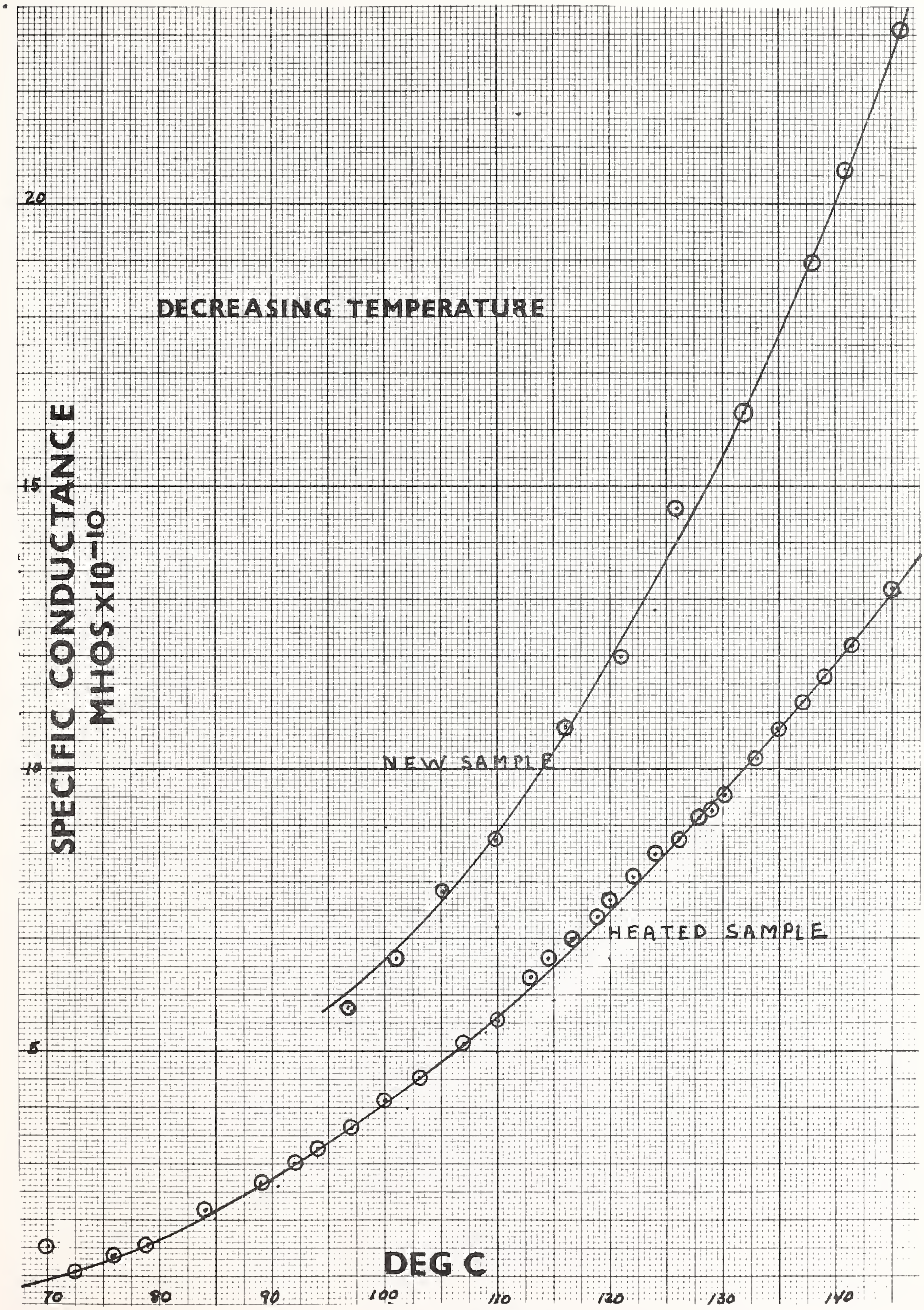
Substituting

$$\sigma = \sum_i \frac{P_i q_i^2}{6\pi D r_i \eta} \tag{12}$$



INCREASING TEMPERATURE
SPECIFIC CONDUCTANCE
MHOS x10^-10
NEW SAMPLE
HEATED
SAMPLE
DEG. C.
5
90
100
110
120
130
140

PLATE 6



DECREASING TEMPERATURE
SPECIFIC CONDUCTANCE
MHOS X10⁻¹⁰
20
15
10
5
NEW SAMPLE
HEATED SAMPLE
DEG C
70
80
90
100
110
120
130
140

PLATE 7

Under conditions of complete dissociation, and ions having unit charge

(13) $$\sigma = \frac{pq^2}{6\pi D\eta}\left[\frac{1}{r_a} + \frac{1}{r_b}\right] = \frac{K}{D\eta}$$

A plot of σ versus $(D\eta)^{-1}$ should be linear. In the case of partial dissociation, the formula

(14) $$\log(\sigma D\eta) = K' - \frac{\phi'}{2KDT}$$

can be derived, where K' is a constant, k is the Boltzmann constant, T is the absolute temperature and Φ' is the Gibbs free energy for the dissociation.

Evaluation of Data

Table (V) gives the observed values of the dielectric constant, conductance, and viscosity as functions of temperature. Plate (8) shows a plot of equation (13) for the SC-250 asphalt.

Conclusions

The ionic constituents in this asphalt behave as if they are completely ionized. The displaced part of the curve corresponds to 100°C at which point water is obviously being driven from the system. The high viscosity of the asphalt prevents ions from recombining once they have been formed. Water is the most prevalent polar and ionic constituent.

No attempt was made to dope the sample with known amounts of water or to determine the absolute amount of water present. It should be mentioned that because of the completely ionized state, the concept of pH has questionable meaning when applied to asphalt.

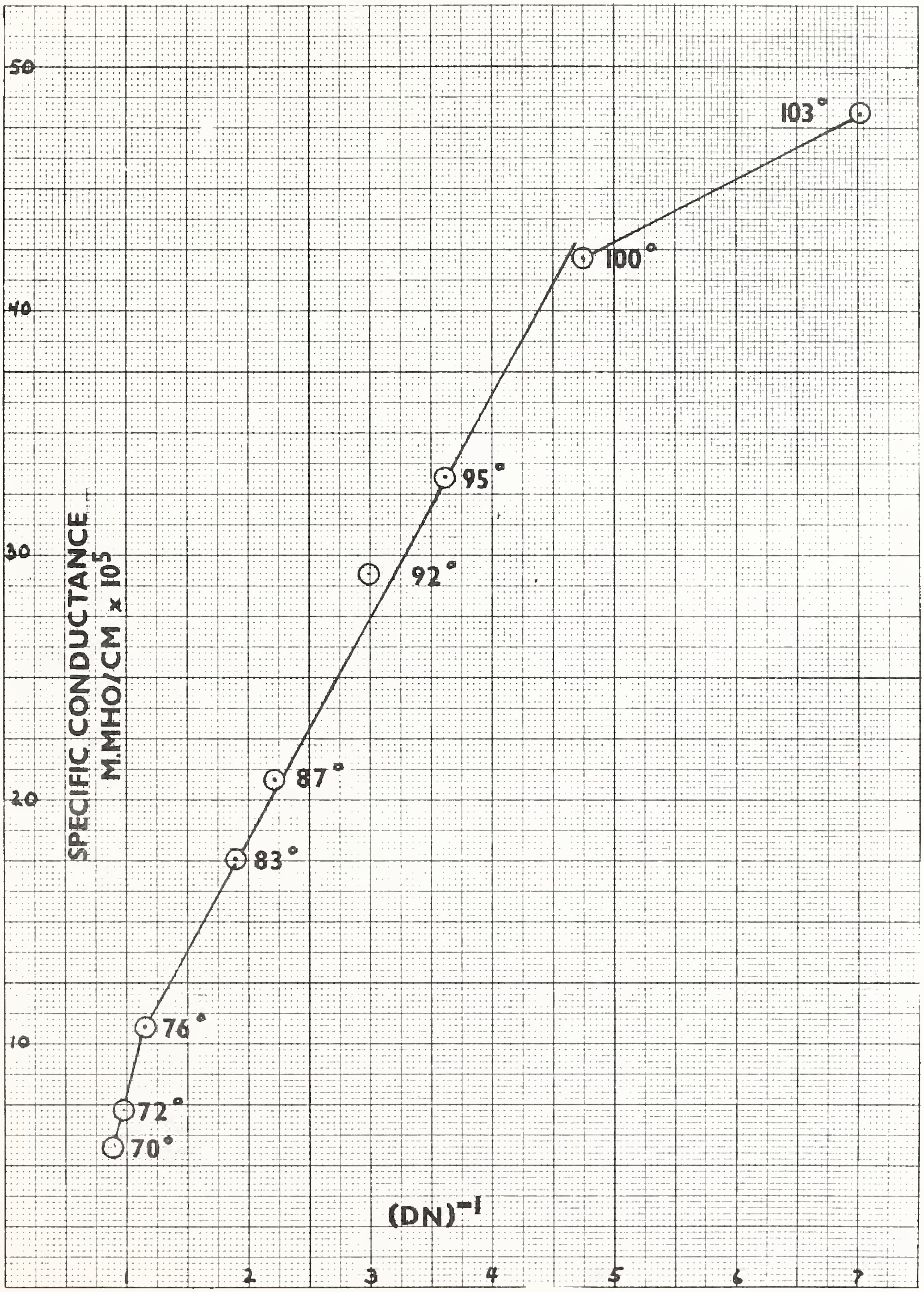


PLATE 8 EQUATION 13

TABLE V

Physical Constants for SC-250 Asphalt

Temp. C°	D	n (Poise)	1/R mhos	mhos/cm.
70	2.814	.3831	.0906	5.790×10^{-5}
72	2.840	.3523	.1142	7.347×10^{-5}
76	2.886	.2970	.1678	1.0795×10^{-4}
83	3.032	.1708	.2737	1.7609×10^{-4}
87	3.127	.1433	.3239	2.0838×10^{-4}
92	3.356	.0987	.4540	2.9208×10^{-4}
95	3.50	.0785	.5157	3.3178×10^{-4}
100	3.91	.0541	.6579	4.2327×10^{-4}
103	4.21	.0339	.7519	4.8375×10^{-4}

pH is defined as the negative logarithm of the hydrogen ion concentration of a solution. pH-meters measure the difference in potential across a thin glass membrane which is due to a difference in concentration in hydrogen ions on the two sides. This potential can be related to pH through the use of appropriate equations and the corresponding pH values can be displayed on the instrument scale. The use of media other than water requires a different calibration equation.

If the pH definition is rigorously applied to asphalt, then according to the last study, the pH becomes an obscure way of indicating the amount of water present in the asphalt. Although this study was not followed any further, conductivity measurements appear to be a significant way to study asphalt emulsions. It should be possible to follow and study breaking points in a very quantitative way.

Part IV THE DIPOLE MOMENT AND MOLECULAR WEIGHT

It is possible to obtain an estimate of the average molecular weight and dipole moment of the polar constituents in asphalt from the theory of dielectrics. Such a calculation was attempted by B. Behl in a paper entitled Asphalt Dielectric as Related to Physical Constitution. The treatment however contains a number of errors. For the Phillips MC-800 asphalt a value of 627 is obtained for the molecular weight along with a value of 2.2 Debye for the dipole moment. These values can safely be regarded as low estimates and may be indicative of association. Infrared measurements indicate a preponderance of 21-23 chain atoms which would correspond to a molecular weight of about 310 (saturated aliphatic), so a dimer would be indicated. The individual moment would then be 1.57 for identical units since this varies as the square root. This is quite large.

Theory

When an electric field is applied across a material, the material becomes electrically distorted. The electrons associated with atoms of the material are pulled in the positive direction while nuclei move the opposite way. Molecules having a positive and negative end i.e a permanent dipole moment tend to orient along the direction of the field.

In a heuristic way, the material can be said to be electrically stretched. In mechanical systems stretching is defined mathematically by an elastic moduli. A similar situation occurs with electrical forces. The "elasticity" in this case is called the polarization.

The polarization which a material undergoes in the presence of electrical forces is composed of three parts; (1) an electronic polarization due to movement of electrons relative to the nuclei about which they belong (P_E); (2) an atomic polarization due to movement of nuclei within molecules (P_A); (3) an orientation polarization due to alignment of molecules with fixed dipole moments along the field (P_O). The relative extent of each type depends intrinsically both on the material and on the nature of the applied electric field. The simplest case occurs when the electric field is due to electromagnetic radiation in the form of light. The field is then sinusoidal with a period of about 10^{-15} seconds. In this short time interval, electrons move but the more massive nuclei and molecules remain fixed. The only contribution is then due to the electrons. This polarization is related to the refractive index by the Lorenz-Lorentz equation:

$$P = \frac{n^2-1}{n^2+2}\frac{M}{d}$$

where n is the refractive index, M is the molecular weight and d is the density. The symbol R is often used to denote polarizations determined at optical frequencies where the refractive index is then equal to the square root of the dielectric constant.

In the infrared region and at lower frequencies nuclei start to move and to contribute to the polarization. This atomic polarization P_A is however less than 10% of the electronic part. The 10% value occurs in the case of hydrocarbons or substances containing large amounts of hydrogen. Nuclei much more massive than hydrogen do not make appreciable contributions. This quantity is difficult to measure since it involves refractive index determination in the infrared region. In the following calculations, P_A will be assigned a value of 10% of the electronic contribution.

The orientation polarization can be obtained from low frequency dielectric constant data by subtracting out electronic and atomic contributions from the total polarization. It determines the temperature dependence of the dielectric constant.

In the case of systems sufficiently dilute so that dipole-dipole interactions can be ignored, the Clausius-Mossotti equation is valid.

$$P_M = \frac{D-1}{D+2}\frac{M}{d}$$

This relates dielectric constant and total polarization. The equation is valid for gases, for non-polar liquids and for very dilute solutions of polar substances in non-polar liquids. Polarizations have the units of volume/mole and are additive.

Procedure

The refractive index for the MC-800 asphalt was obtained with an Abbe temperature controlled refractometer by extrapolating to 100% the refractive index of a number of solutions of asphalt in typewriter oil. The value of n so obtained was highly reproducable. For the MC-800 asphalt n is 1.479 and d is .978 g/ml at 23 deg.C. Solutions were made of asphalt in carbon tetrachloride

and the dielectric constant of these was determined.
The ratio $D-1/D+2$ was plotted as shown and extrapolated to zero concentration in accordance with the dilute solution restriction. Similar data is also shown for a Kevin asphalt although calculations were not performed on it. The MC-800 data is given in table VI.

The refractive index and density of the carbon tetrachloride were obtained. ($n^2 = 2.128$; $d = 1.583$; $M = 153.84$

<u>Calculations</u>

$$P_M = P_0 + P_A\,(\text{asphalt}) + P_A\,(CCl_4) + R_M\,(\text{asphalt}) + R_M\,(CCl_4)$$

The extrapolated value of R_M(asphalt) is zero and the atomic polarizations will be taken as 10% of the electronic contribution. Introducing these simplifications and dividing by the molecular weight yields:

$$\frac{P_M}{M} = .174 = \frac{P_0}{M} + \frac{1.1\,R_M\,(CCl_4)}{M} = \frac{P_0}{M} + \frac{(1.1)(25.6)}{M}$$

In order to obtain an estimate of M a value of P_0/M must be obtained from the pure asphalt. The total polarization can be obtained from the dielectric constant and the electronic part can be obtained from the refractive index. In calculating the total polarization from the dielectric constant the choice of D value i.e the temperature becomes critical. At low temperatures, interactions prevent any permanent dipoles present from aligning with the field and the orientation polarization is consequently nearly zero.

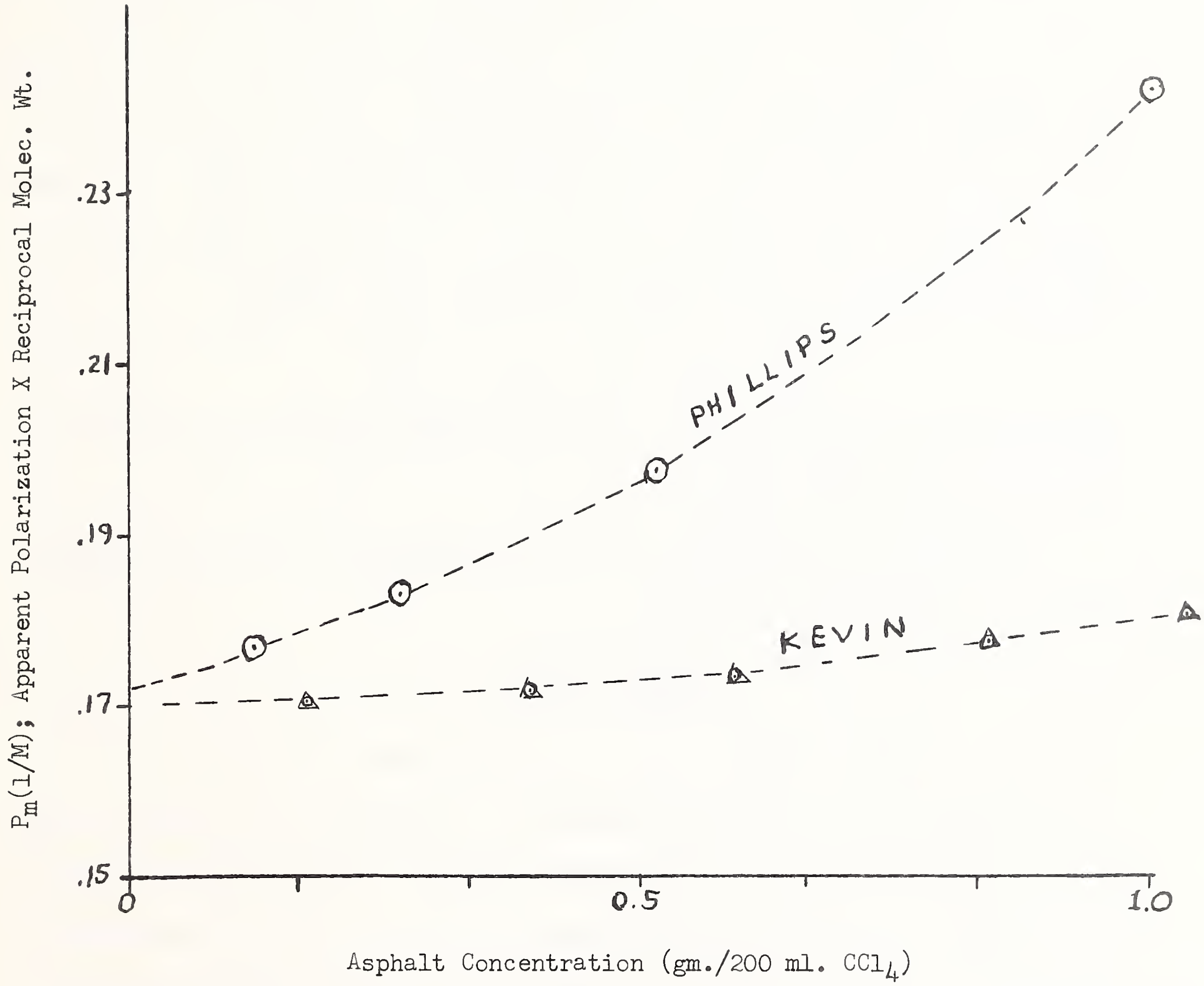


PLATE 9 EXTRAPOLATION TO ZERO CONCENTRATION

TABLE VI

Asphalt Conc.	D	P_m/M
0.121 gm/200ml	2.175	.1775
0.263 gm/200ml	2.23	.1836
0.510 gm/200ml	2.37	.198
1.00 gm/200ml	2.875	.243

Also, at low temperatures, dipole-dipole interactions prevent the use of the Clausius-Mossotti formula. From a graph of dielectric constant versus temperature (Plate 3) the dielectric constant has a maxima of 3.33 at about 90 deg. C. At higher temperatures, the order-dissorder transition which occurs at 90 degrees results in miss-alignment of the dipoles. The value of 3.33 is used with the reservation that this is a low value and that some dipole-dipole interactions still probably exist. A better procedure which was not done would have been to extrapolate solutions of asphalt in carbon tetrachloride to unit asphalt concentration. This value, with a density of .978 for the asphalt yields a value of P_M/M of .446. Then:

$$\frac{P_O}{M} = .446 - .289 - .029 = .128$$

Substitution of this value into the previous equation for the solutions then gives a molecular weight of 627.

The Langevin-Debye theory predicts a dependence of orientation polarization on temperature such that:

$$P_O = \frac{(4)\ (3.14)\ Nu^2}{9kT}$$

Where N is Avagadros number, u is the dipole moment, k is Boltzmann's constant and T is the absolute temperature. Theequation is valid only when there are no interactions present in the system. It is for an ideal gas of point dipoles of moment u. If this equation is used, the calculated value of u will be very low, but it can serve as an estimate. Substituting for P_O and solving for u yields a value of 2.18 Debye.

PART V DIELECTRIC CONSTANT FOR PENETRATION ASPHALTS

The dielectric constant was also obtained as a function of temperature for a number of penetration asphalts. In this case the treatment given in the previous section is not valid except at elevated temperatures. In the temperature range below 100 deg. C. asphalt behaves as a more or less typical crystalline solid as far as dielectric effects are concerned. For a dipolar solid a number of preferred orientations exist within the lattice. As the temperature is increased, the potential energy difference between these orientations is lessened and transitions between these states become more prevalent. The dielectric constant is determined by the relative orientation of these states and their populations.

In the low-temperature region applying an electric field results in a decrease in ordering in the system since molecules were originally in a highly ordered state in the crystal. As temperature is increased the ordering is decreased. At some point, applying an electric field actually increases the ordering in the now disordered system. At this point the dielectric constant has a maximum value and its slope changes sign.

A dielectric constant curve with a maxima in it is then idicative of solid behavior. The transition temperature at which the maxima occurs is either below or at the melting point. The presence of such order-disorder transitions in the penetration asphalts is indicated on the following graphs.

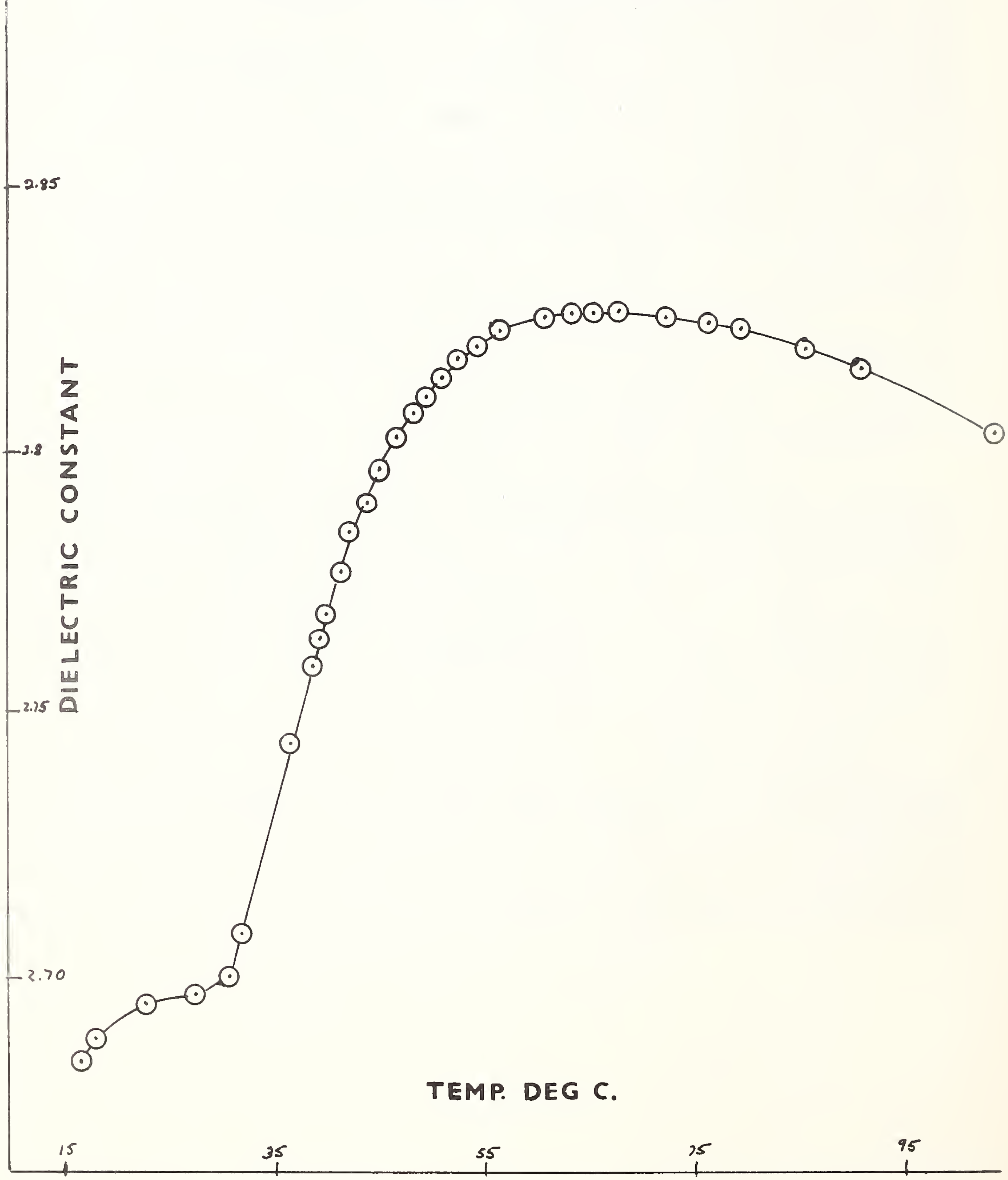


PLATE 10 D vs T HUSKY P_2O_5 BLOWN

PLATE 11 CONOCO 100-120 PEN

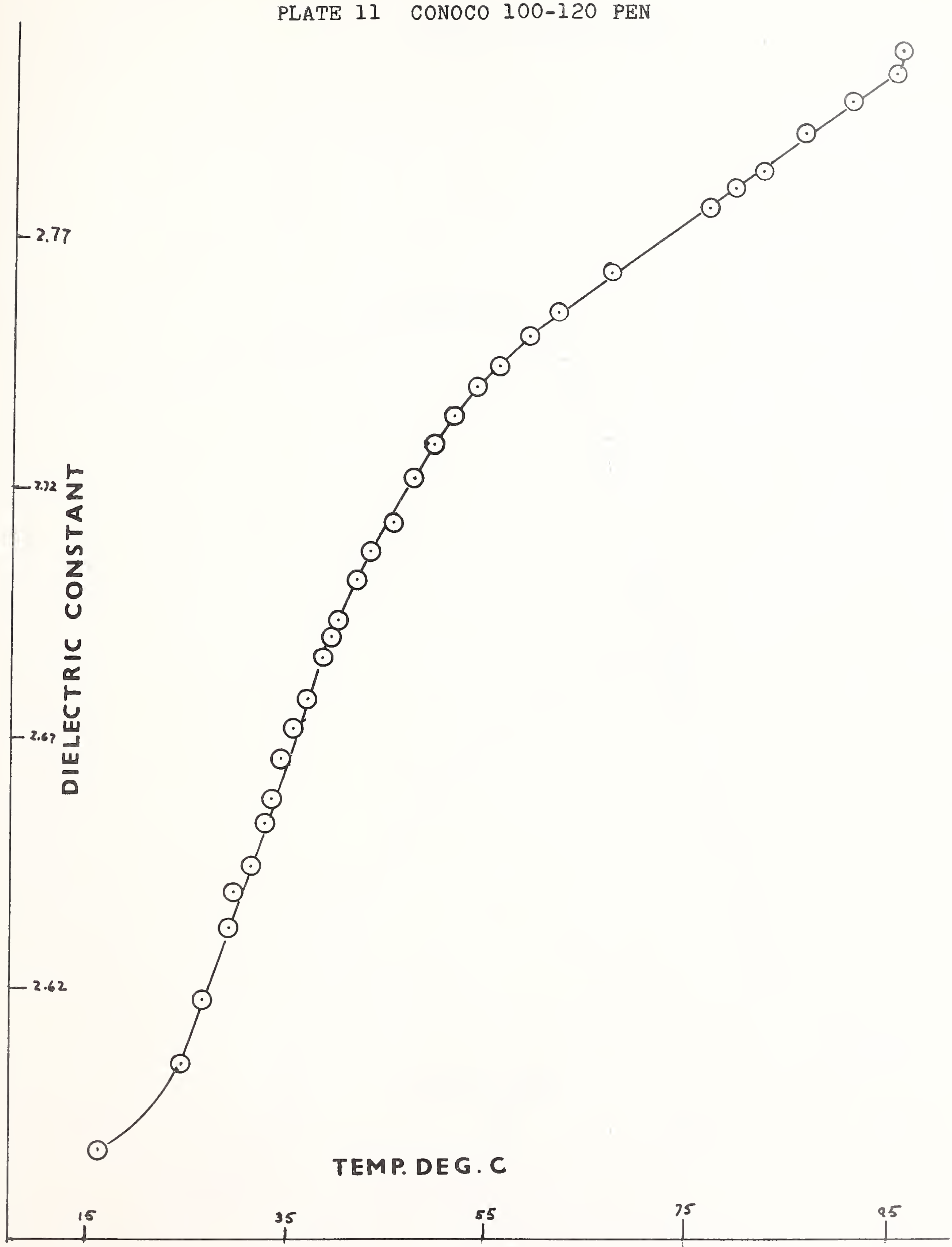


PLATE 12 KEVIN 110 PEN

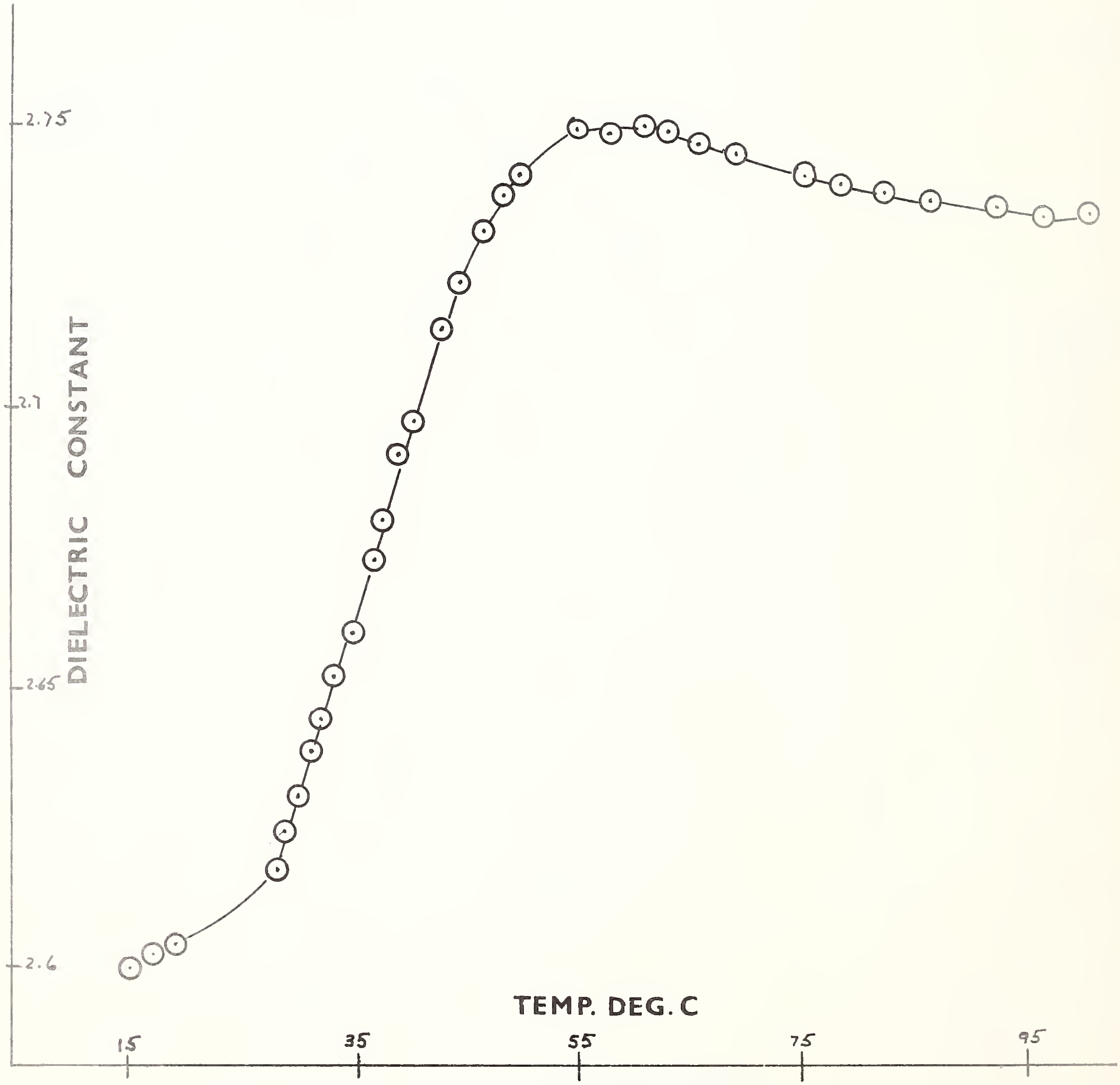
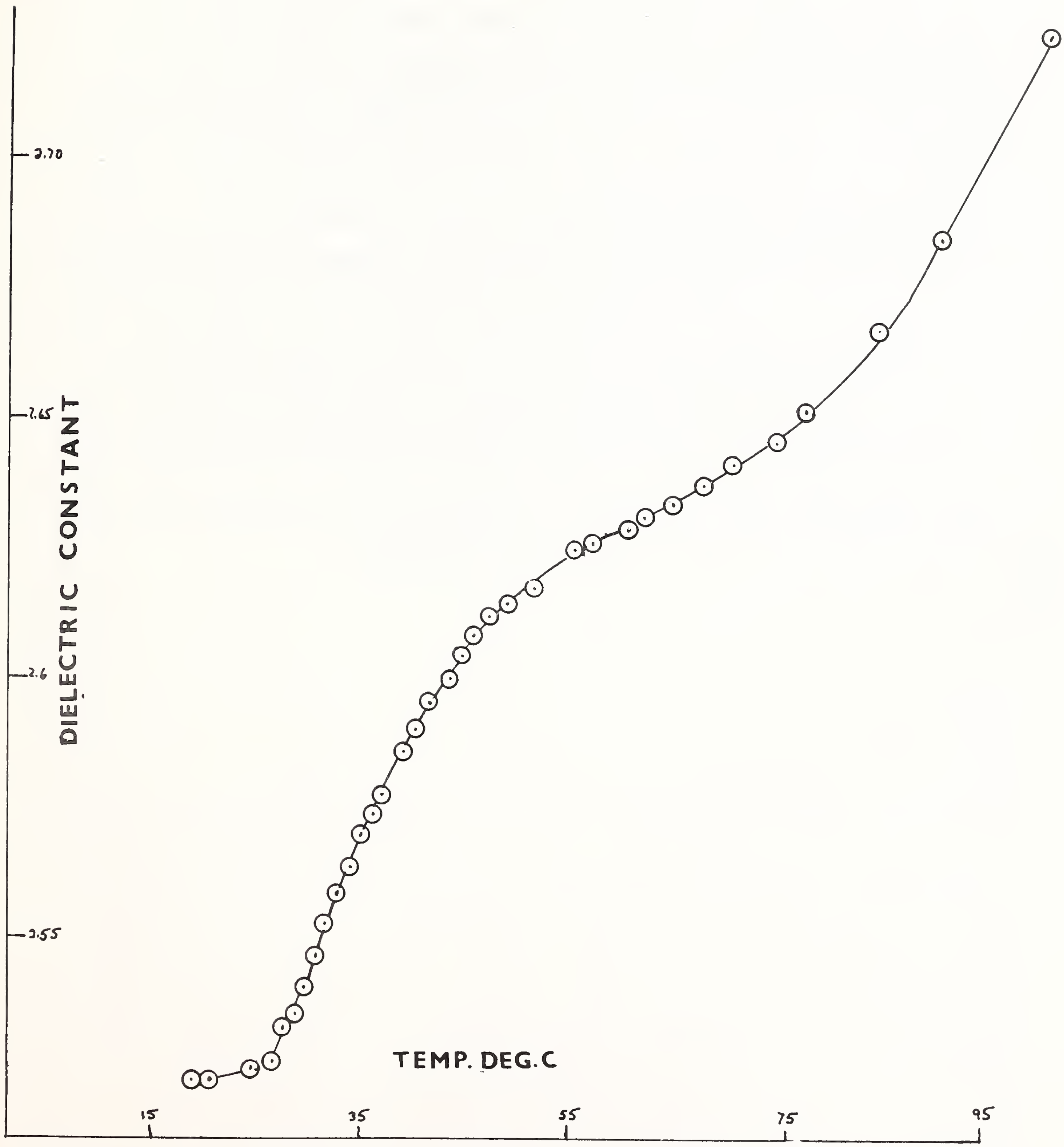


PLATE 13 PHILLIPS 100-120 PEN



It is instructive to plot the total polarization as a function of temperature for a series of asphalts, although no simple equation exists between the polarization and the temperature except in the case of the point-dipole gas (Langevin Debye). When plotted in this way, the slope can be interpreted as an effective dipole moment. The systems behave as if the dipole moment were continually changing. Polarizations are also additive which means that the electronic and atomic contributions merely shift the vertical scale factor. Comparisons of absolute magnitude are not valid since the molecular weight is also an unknown scale factor. The graphs for the Phillips MC-800 asphalts show a temperature dependence that is exponential and due to decreasing viscosity. It was first thought that the decrease in dielectric constant with increasing temperature could be due to dissociation of associated components however a calculation of the curve for this effect yields much too small a slope to be effective over the temperature range measured. The maxima are due to order-disorder, or second order phase transitions within the material.

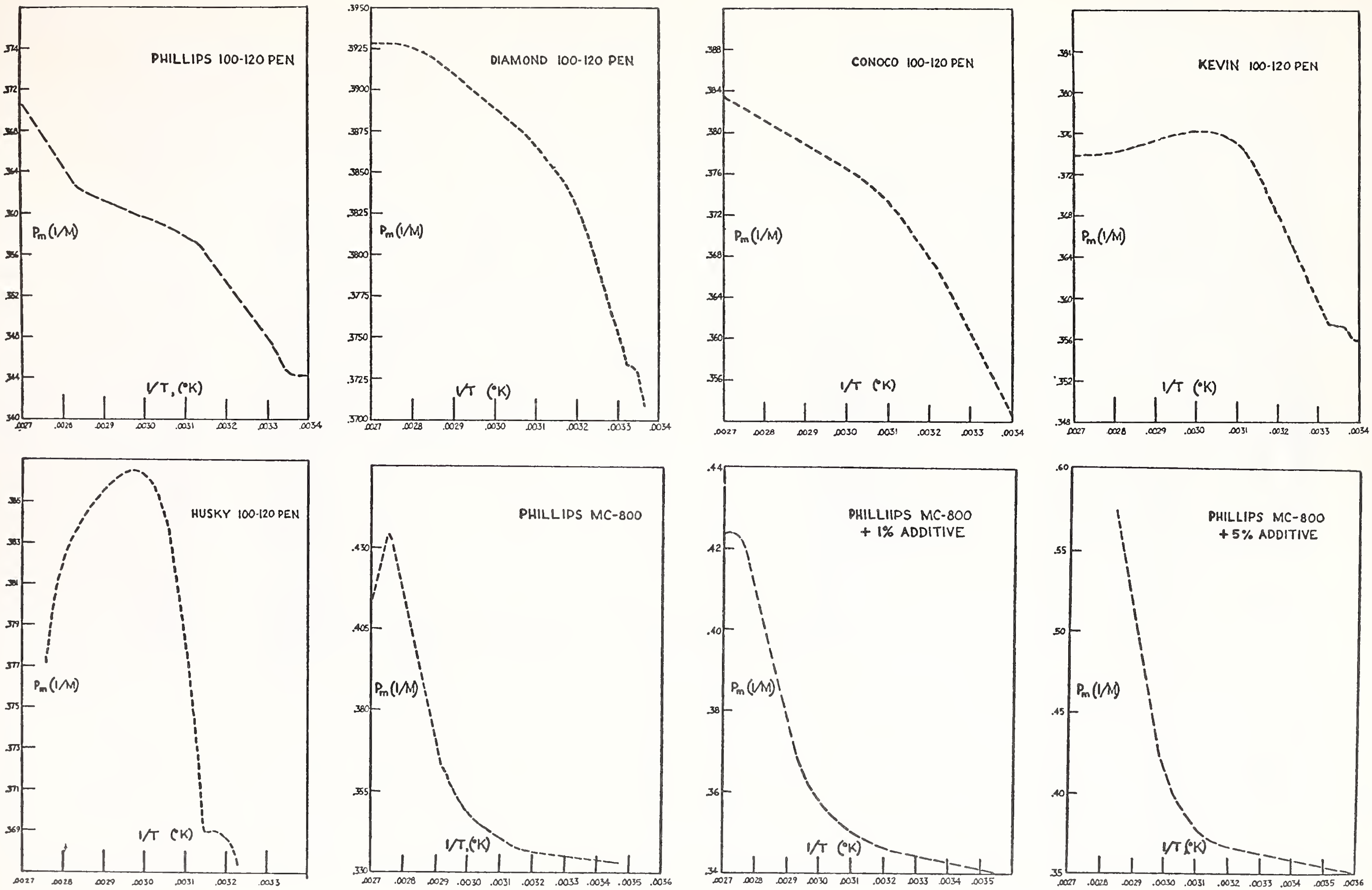

PHILLIPS 100-120 PEN
DIAMOND 100-120 PEN
CONOCO 100-120 PEN
KEVIN 100-120 PEN
HUSKY 100-120 PEN
PHILLIPS MC-800
PHILLIIPS MC-800
+ 1% ADDITIVE
PHILLIPS MC-800
+ 5% ADDITIVE
Pm (1/M)
1/T (°K)

PLATE 14

Measurements were also made to determine the effect of an adhesive agent on the dielectric constant. The following plate is taken from the paper by B. Behl. An activation energy for rotational motion could be computed for each of the curves as was done in the previous section. As indicated in the diagram, the general effect of the agent seems to be an increase in both the dielectric constant and in its susceptibility.

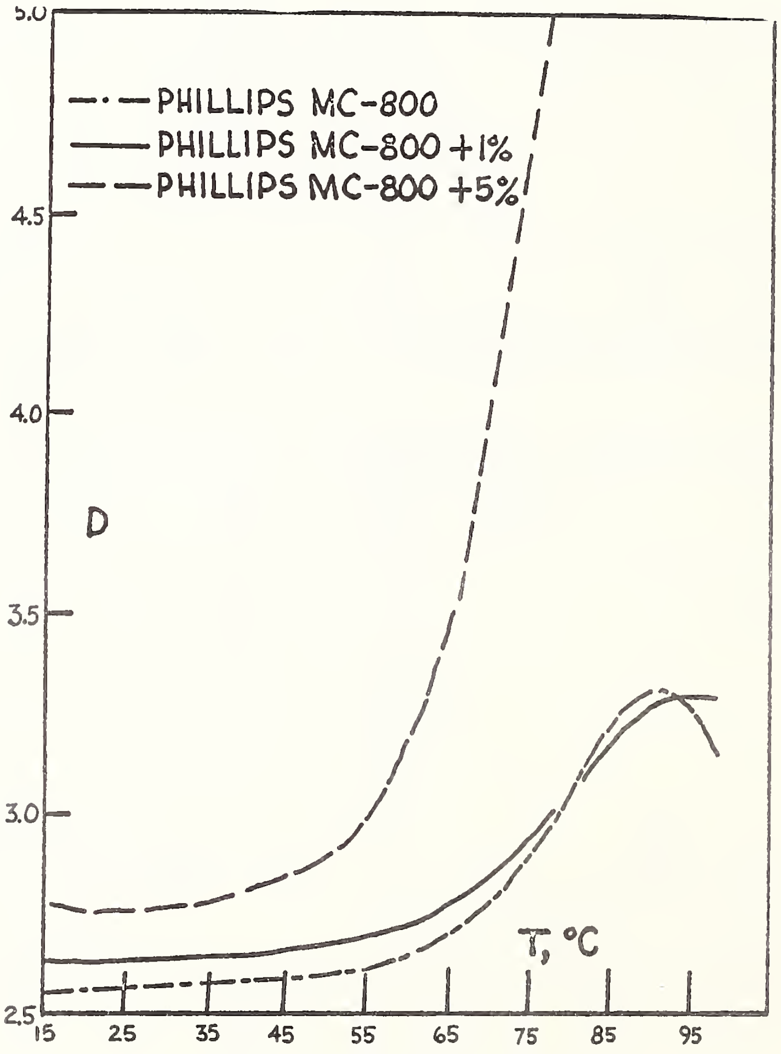


PLATE 15 EFFECT OF ADHESIVE AGENT

PART VI General Conclusions and Applications

Table (I) compares various bonding energies. The value of 2.72 Kcal/Mole places the interactions in the amine category or somewhere slightly above. The value of 4.6 Kcal/Mole compares favorably with that for water in a solid lattice. Table (II) would indicate bond energies from one to three Kcal/Mole if one assumes six neighbors. The heavier asphalts may have a greater degree of crosslinking which could mean that the bond energies are the same but the number of bonding sites, that is, the coordination number is larger. The number of bonding sites should vary as the square of the molecular radius, proportional to the surface area. From the energy variation we expect the molecular radii to differ by a factor of 1.5 at the most between the lightest and heaviest asphalts. The mean molecular weight should vary by about the same factor. A larger molecular weight and greater crosslinking should result in a more brittle product. The cohesiveness of the material, however, should depend primarily on the internal bonding energy while elasticity depends on chain length.

The Role of Water in Asphalt

As indicated, water probably plays an important role in the properties of asphalt. A very fine emulsion of 60 percent water and 40 percent asphalt was prepared by using a Waring blender and was stable over a period of time greater than six months, after which it was discarded. The emulsion had an oily texture and showed no tendency to adhere to glassware or to the hands.

Water is a Lewis base which means that it can contribute a pair of electrons to another substance (Lewis acid) to form a bond. If water can be bonded in asphalt as indicated (perhaps in ionic form) then this implies that the asphalt behaves as a Lewis acid. The addition of a stronger Lewis base than water to asphalt should result in a displacement of the water and

the formation of different intermolecular bonds. Amines and salts of oleic acid have found use in asphalt as adhesive agents. The oleate ion is a strong Lewis base as is the amine. The addition of fatty acid amines to asphalt results in a stiffer product, as well as greatly enhancing the adhesion to stone.

While average bond energies have been given, there are undoubtedly numerous sites in the material showing much higher energies. The most basic constituents in the asphalt would tend to accumulate at these positions after sufficient periods of time. The amine would displace water from these positions with a subsequent increase in crosslinking. These positions probably also play a major role in the penetration of water through asphalt.

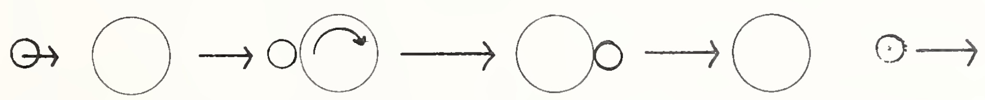
The Nature of Stripping

A number of bonding mechanisms are possible between asphalt and stone aggregates. When asphalt is initially coated on stone, the most likely interactions are those between the stone and the hydrogen atoms on the organic constituents of the asphalt. If the mixture is then brought in contact with water, some of the water dissolves in the asphalt and is displaced progressively throughout the asphalt via hydrogen bonding in the material and may result in a rapid build up of water around the surface of the rock. Any free diffusion of water or of any material through the asphalt would be very slow due to the very high viscosity. As water gradually accumulates around the rock, the bonds between the organic constituents of the asphalt and the rock are broken and are replaced with a water crosslink. The extent of this depends on the relative Lewis acid strength of the asphalt and the rock. A few predictions are possible. Much higher electrical forces exist about a silicate than do about a carbonate. Silicate material should show

greater Lewis acid strength than a carbonate. The accumulation of water at the interface should be much larger. As the accumulation of water proceeds, adhesive forces should gradually increase until a monolayer is formed, since the water aggregate bonds are stronger than those between asphalt and aggregate. With greater amounts of water, the adhesion between the rock and asphalt diminishes due to a lack of cohesion between water and water. Upon agitation, the asphalt would then be easily stripped from the rock.

In practice, silicates show much poorer adhesion than do carbonates. Hydrous silicates such as flint are especially poor. Also freshly crushed silicates show much higher adhesion than material which has been allowed to stand. This may be due to an accumulation of water on the surface of the material from the atmosphere.

It is possible to explain moisture penetration by a progressive displacement mechanism (Grotthus conduction). This mechanism is common in hydrogen bonded systems and accounts for certain types of diffusion. Essentially it is simply an association of two molecules followed by a rotation and then a dissociation. The smaller group is the one that moves. This is illustrated by the following diagram.



This mechanism permits diffusion in systems such as solids where free translation is not possible. Since rotation is possible only above a certain critical temperature in the asphalt, we cannot expect appreciable moisture penetration or stripping to take place at low temperatures. The dielectric constant measurements provide a good estimate of this temperature. For the SC-250 it is 65°C. Below this temperature, moisture penetration should take place only over very considerable periods of time. With appropriate equipment, one could measure the diffusion of water through asphalt and then

calculate this time. It should also be possible to get the rotation transition temperature by this method.

Amines as Stripping Preventatives

The addition of amines to the asphalt does several things. (a) It displaces water as a cross linking or hydrogen bonding agent. (b) It ties up acidic components in the asphalt involved in the progressive displacement mechanism. (c) If present at the interface, it will act as a coupling or cross-linking agent. It must be emphasized that the third effect is necessarily small. The commercial fatty acid amine adhesive agents are used in concentrations of about 0.1 percent or less and this is dispersed throughout the bulk of the asphalt. The large molecular weight and size of these amine molecules prevents any migration or displacement through the very viscous asphalt. Under these conditions only one out of every thousand molecules in contact with the rock could come from the adhesive agent. The bonding energy between the amine and the rock can be at most four or five times greater than that between the normal asphalt components and the rock. This would indicate an increase in adhesion of 0.5 percent which is negligible. Experimentally, the addition of 0.1 percent amine may increase the adhesion by a factor of four or five. Treatment of the rock with the amine prior to mixing may prove more effective since any water present would be displaced and since the surface amine concentration would then be large.

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PART I-B INFRARED STUDIES OF ASPHALT

Infrared Spectrophotometer

Technique and application of the IR7 to asphalt has been one of the prime objectives. Coupled with the normal operational adjustment of the instrument, sample preparation and interpretive procedures have been investigated. In order to obtain usable information, the instrument must be adjusted for limitations of the sample, while at the same time, interpretation requires a high level of spectral resolution.

For high resolution work, the investigator is normally forced to work at a slow speed which is impractical. It has been found that asphaltic samples produce useful data discontinuously and there are large areas of uninformative non-absorptive regions. However, within each order there exists an area of importance. By the use of automatic speed supression, scanning speed can be maintained at a rapid and efficient rate for scanning of the non-absorptive regions, and for areas where significant absorption occurs, the scanning speed is automatically reduced for effective resolution. Through the use of this feature of the instrument, it was possible to efficiently and effectively scan the entire region.

Asphaltic samples normally produce a relatively weak series of absorption peaks in the first order, while significant absorption peaks in the third order are generally very intense. Thus, for usable results in the areas of weak band spectra, a relatively long sample path is required, while for interpretation of the third order, a much smaller sample path is desired.

Another feature of the IR7 is the scale expansion. Where a close study of a portion of a curve is desired, and 4% of the recorder ordinate can be expanded to full scale. With the appropriate use of this feature, many shoulders which occur in the areas of deep absorption were clarified.

To establish broad peaks of very low intensity, the technique of noise, integration was applied. This was done by use of the repetitive scan feature of the spectrophotometer.

Total Asphalt Spectra

Three samples of asphalt were initially submitted to Connecticut Instrument Company for purposes of determining an effective instrument and method for Infra-red analysis.

An attenuated total reflectance, (ATR), attachment was utilized with a Beckman 4 infra-red spectrophotometer for direct analysis which eliminates certain preparation problems.

The following spectrographs are for the asphalt samples:

Fig. 1. Diamond; vacuum distilled asphalt

Fig. 2. Conoco; solvent refined asphalt

Fig. 3. Kevin; cracked asphalt

Some of the important groups of asphalt were identified according to the wave length of absorption peaks. Thus, a method was established for functional group analysis of asphalt components. It can be noted from the spectrographs that a similarity of groups exists for the Conoco and the Kevin asphalt samples. The following observations were made on the samples:

Diamond Asphalt: Few (OH) groups, lesser aromatic vibrations and aromatic substitution.

Conoco Asphalt: Higher (OH) concentration, higher concentration of aromatic substitutions and aromatic vibrations.

Kevin Asphalt: Greatest (OH) concentration, but lesser aromatic substitutions as compared to Conoco.

It is evident from the three spectrographs that their constituents are very different although the physical measurements of viscosity,

PLATE 1

Fig. 1. Diamond

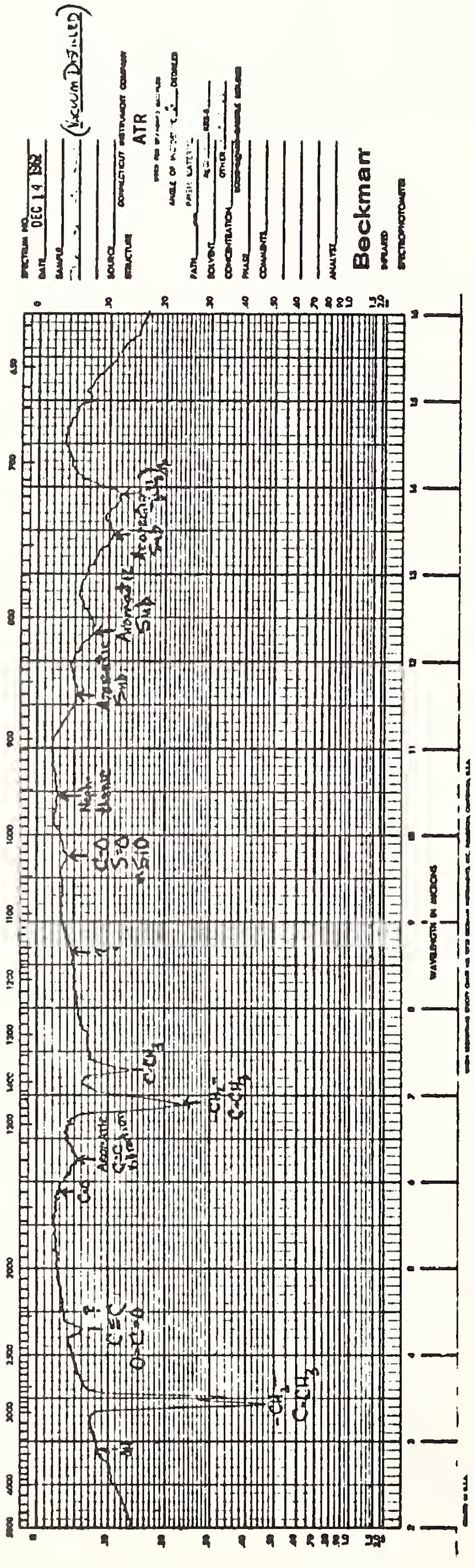


Fig. 2. Conoco,

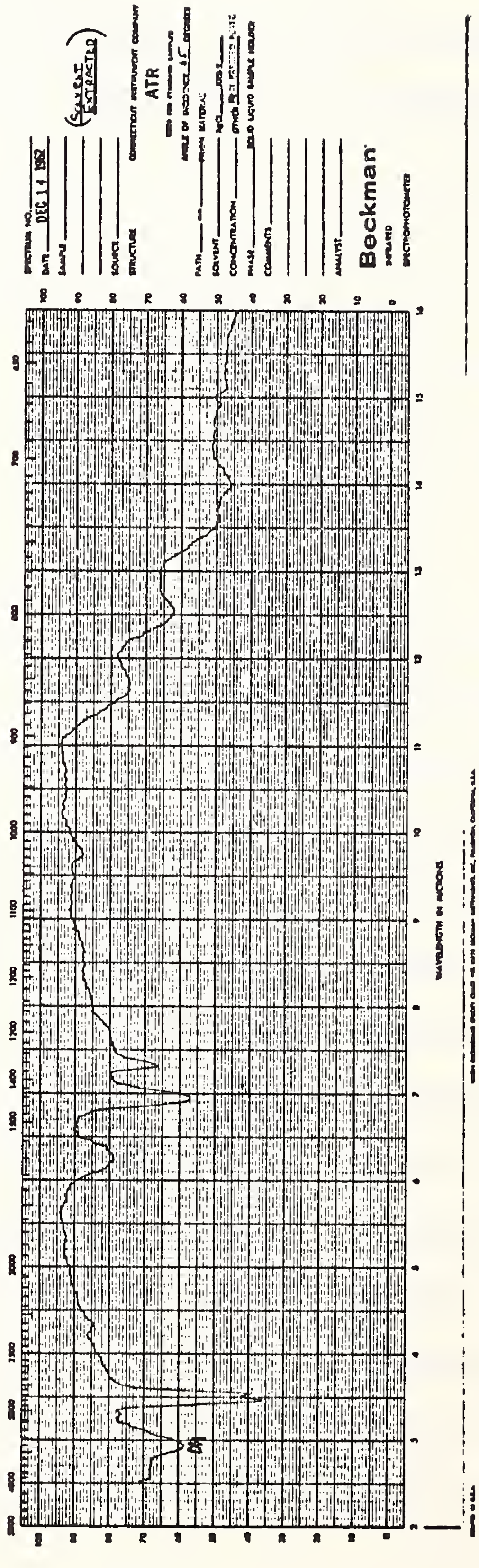
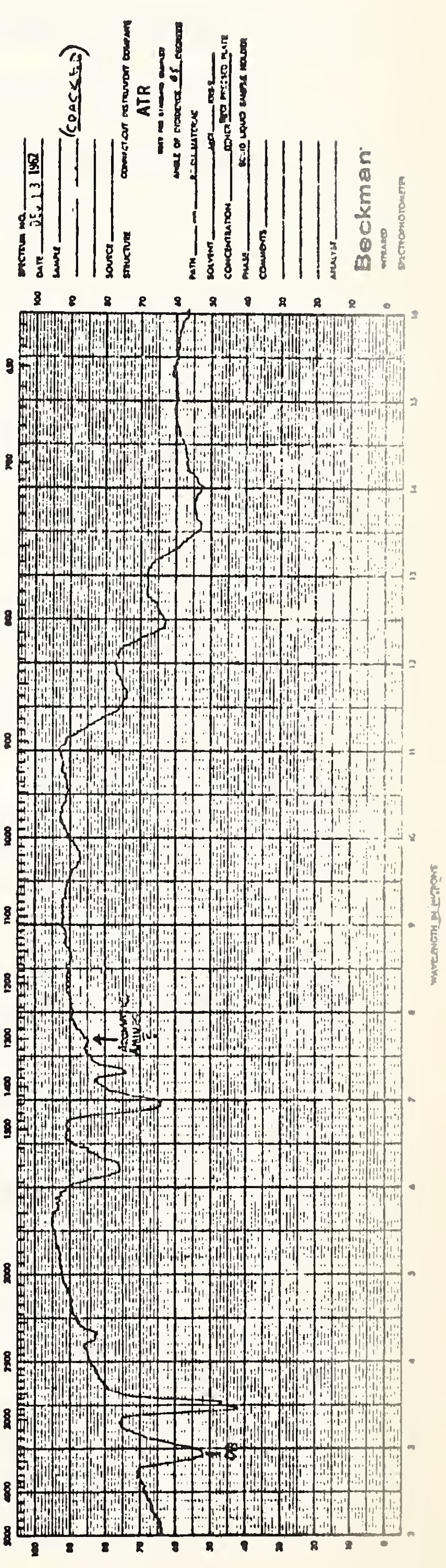


Fig. 3. Kevin



ductility, etc., may be identical. These charts are included since they are A.T.R. charts. In subsequent work, a solvent such as carbon tetrachloride is used or the spectra are obtained by transmission rather than by reflectance methods. No A.T.R. studies were done under this project. There are certain slight shifts in spectra between the transmission and reflection methods.

SAMPLE PREPARATION METHODS

Probably the greatest problem was in sample preparation. Little had been done toward developing techniques to handle asphalt. No one technique developed thus far has been able to produce the desired data in all areas. Methods which have proven fruitful are as follows:

1. Thin Film Preparation

Thin Film asphalt samples are made by compression of asphalt between two untreated cellophane sheets. The Carver Press hot plate supplies both heat and pressure for the compression.

It was found necessary to outline a general procedure for each type of asphalt encountered. An exact method can only be arrived at through experimentation.

With lighter, less viscous asphalt, volatilization occurs at lower temperatures. Also, less time can be tolerated under pressure before bubbles and thin spots appear.

After a satisfactory thin film has been produced, it is transferred to a sodium chloride (NaCl) plate for infra-red analysis. With this procedure, a thin film can be prepared without the use of a solvent.

The following methods have thus far produced satisfactory samples for transfer to a salt plate:

Phillips 84 Pen asphalt:	100° C 30 seconds 2000# pressure
Phillips 100-120 Pen asphalt:	100° C 30 seconds 1000# pressure

MC 250: room temperature
30 seconds
1000# pressure

SC 250: room temperature
30 seconds
1000# pressure

MC 800: room temperature
30 seconds
1000# pressure

Mounting thin films of the more viscous asphalts without using a salt plate has proven unsatisfactory. The heat from the IR source causes even 84 Pen asphalt to run, thus rupturing the film.

The Carver Press method has produced films for transfer to salt plates which are thin enough for analysis of the CH stretch region. This analysis has formerly been impossible to perform on the more viscous asphalts without the aid of solvents which may cause alterations to the asphalt.

2. <u>Procedure for KBr Preparation</u>

Because of its hygroscopic nature, extreme precautions must be taken with KBr in order to prevent an energy loss in the third and fourth orders. Reagent grade KBr has a quantity of moisture in the crystalline structure as well as water contamination occuring during the handling, weighing, and grinding of KBr. The following method eliminates the crystalline water as well as any water incorporated during preparation:

A stock of KBr is ground fine enough to use in the die and placed in a muffle at approximately 700° F for two hours. It is then placed in storage in an oven at 260° F. A sufficient quantity of muffled KBr should be on hand at all times. Only an amount necessary for one pellet is removed from the oven at a time. Any excess KBr removed should be placed in a container marked "To Be Muffled". When a sufficient quantity has been accumulated in this container it is to be remuffled and the contents added to the usable KBr.

The sample to be prepared in a KBr pellet is handled in the following manner: A sufficient quantity of the unknown to facilitate grinding is ground and dried in the 260° F oven for 15 minutes. A quantity of KBr and the unknown are removed and cooled in a dessicator. 0.4000 grams of KBr and 0.0005 grams of the unknown are weighed and thoroughly mixed with the agate mortar and pestle. This mixture is then dried in the 260° F oven for 15 minutes. Immediately after drying, the KBr pellet is to be prepared using the procedure given in the instruction manual for the KBr die. The completed pellet should then be stored in the 260° F oven for at least 24 hours. Immediately prior to running the sample in the IR, the pellet is to be dessicated and weighed. All weights, sample destination, date of preparation, and special instructions should accompany the sample at all times. This technique allows the examination of solid samples such as aggregate. The disadvantages are: length of time necessary to produce samples and limitation to solid samples.

3. <u>Ring Method</u>

A wire ring is dipped into the asphalt, then withdrawn slowly so that a thin film is supported across the ring. The advantages of the

ring method are: extremely short sample path length, no solvent necessary and speed of preparation. The disadvantages of the ring method are: sample path not reproducible, sample path unknown, maximum surface oxidation, and the limitations imposed by sample viscosity.

4. Slurry

The sample is spread uniformly on the sodium chloride plate. The advantages of the Slurry method are: No solvent interference in the spectra, extremely thin film obtainable, and ease of preparation. The disadvantages of the Slurry method are: an unknown and non-uniform sample path length, and non-reproducibility of the path length.

5. Liquid Sample

The sample is dissolved in an appropriate solvent and placed in a liquid cell. Advantages of the liquid sample are: the ability to vary concentration and the ability to vary sample path length. The disadvantages of the liquid sample are: possible solvent sample reaction, time requirement for sample preparation and solvent interference in the spectra. It has not yet been possible, through the use of a reference cell containing the solvent to completely cancel out the solvent spectra. This is an inherent difficulty in infrared analysis since infrared intensities are much lower than visible light intensities for all known polychromatic light sources.

Slide Analysis Procedure - Asphalts

A sample is placed on a salt (NaCl) plate and thickness adjusted to read approximately 20% transmittance at the 1600 cm^{-1} position. All orders are run at this sample thickness.

Sample is then thinned to read 25% at the 1375 cm^{-1} region. Orders 1 and 2 are re-run. Orders 3 and 4 are run with sample further thinned to

read between 10% and 20% transmittance at the 2927 cm^{-1} peak. The scanning speed is slowed from 80 cm^{-1} per minute to 20 cm^{-1} per minute between the wavenumbers of 2800 to 3100 on this last run.

Selection of Solvent

The first consideration for a solvent to be used in Infrared spectroscopy is its transparency to Infrared radiation. Thus, ideally, the solvent would be free of absorption frequencies from 600 cm^{-1} to 4000 cm^{-1}. Solvents of this nature are not obtainable if known. Thus it is necessary to select solvents which will be transparent in the wave number region desired for study. Since we are working in the area of asphalt, it is desirable to have solvents which are transparent in those regions of asphalt absorption bands. It is advantageous to have solvents which are transparent in areas which are also transparent in asphalt. It is necessary to have an appropriate solvent for asphalt. Two compounds which suggest themselves are carbon tetrachloride and carbon disulfide. Both are good solvents for asphalt and both have large areas of transparency in the asphalt absorption areas. Carbon disulfide, however, has many disadvantages which are not shared by carbon tetrachloride. Carbon disulfide will contaminate the sodium chloride windows to the extent that grinding is necessary to remove this contamination. Also, disulfide presents additional safety hazards. While carbon tetrachloride is relatively transparent in the 2800 to 4000 wave length region, it dones, unfortunately, exhibit a very weak broad absorption in the neighborhood of 3000 wave numbers. This absorption band becomes more pronounced as the cell length increases. This is not a critical situation since the "law of additivity" applies. This is an extension of Beer's law which states that the absorption of radiation by one species will be unaffected by the presence of other materials whether they absorb or not. Thus for a two component system $A_{solute} = A_t - A$ solvent.

The Marcusson Separation Method

Asphalt can be separated into a number of components by solvent separation techniques. Phillips 84 Pen asphalt was separated by the Marcusson Method and the components subjected to infra-red analysis.

1. Asphaltenes removed with normal pentane. Dried to constant weight.
2. Pentrolenes (oils and resins) treated with dired fuller's earth.
3. Oils extracted from fuller's earth with normal pentane. Pentane distilled off and oils dried to constant weight.
4. Parts of resins extracted with thiophene free benzene. Balance of resins extracted with chloroform. Solvents distilled off and resins dried to constant weight.

NOTE: Fuller's earth might cause some chemical change in molecular structure of resins.

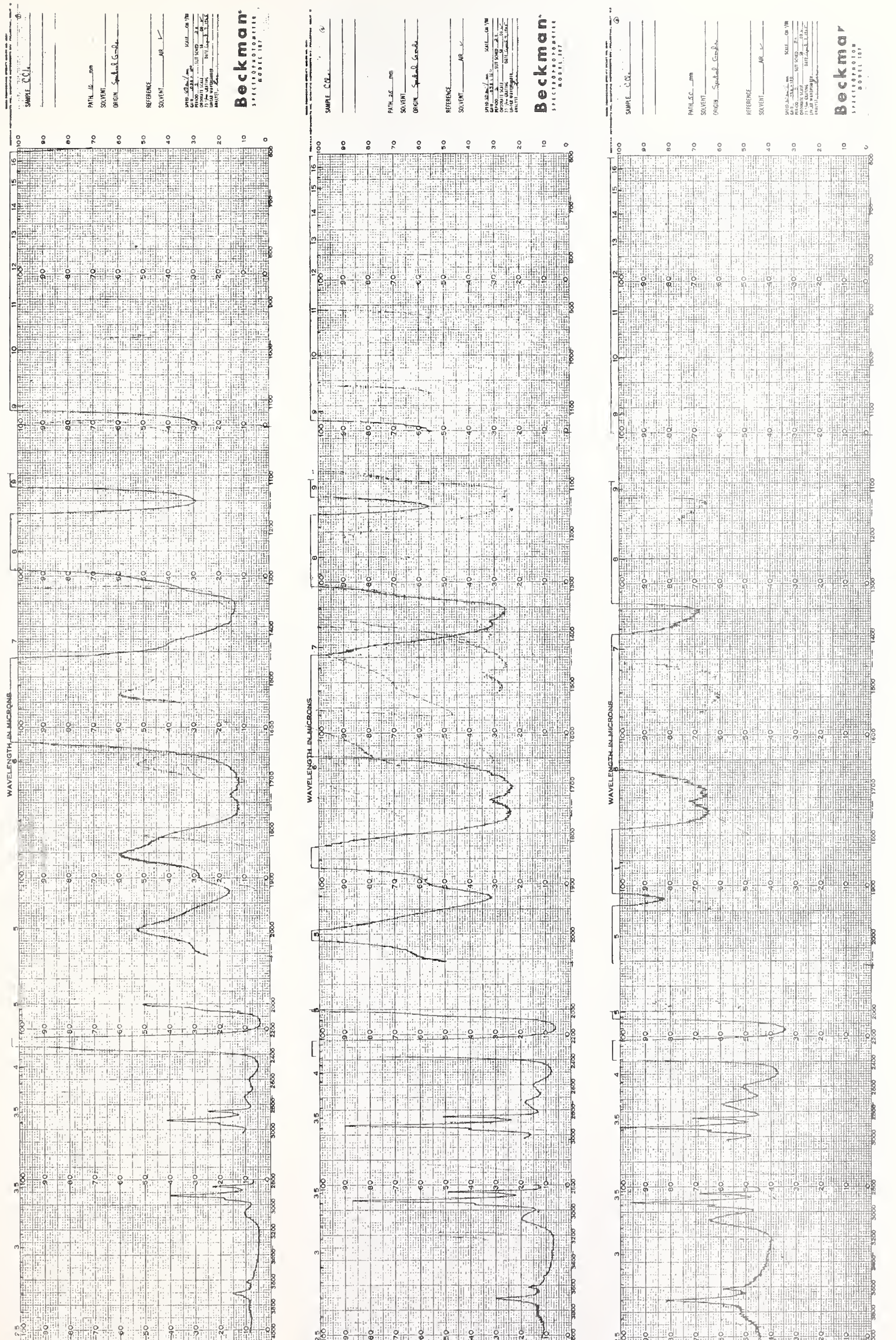


PLATE 2 Carbon Tetrachloride Spectra

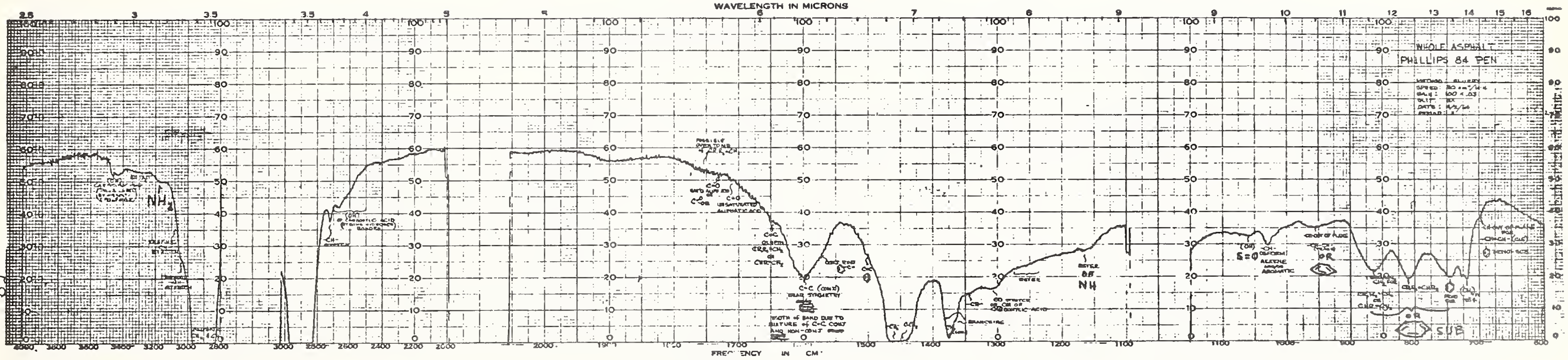


PLATE 3 Whole Asphalt Phillips 84 pen

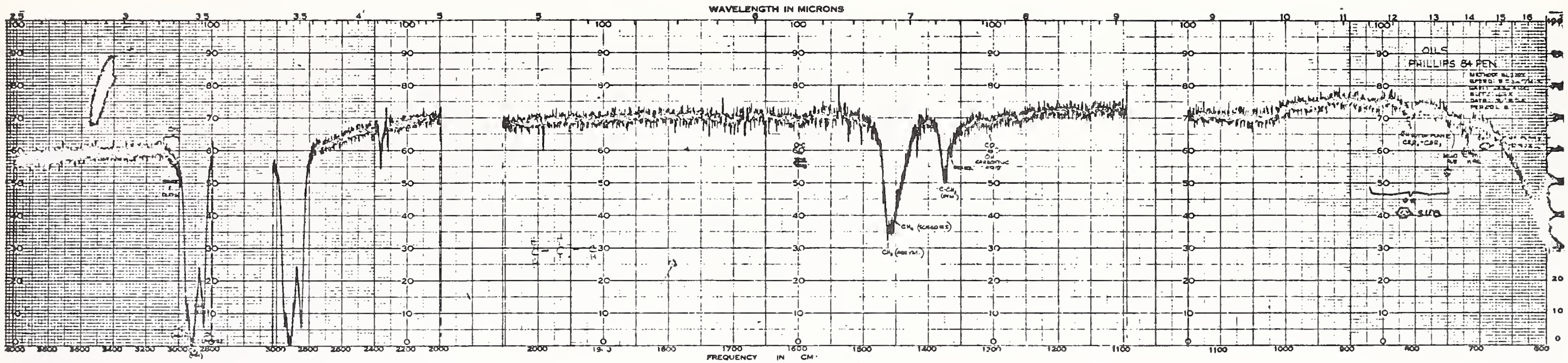


Plate 4 Oils Phillips 84 pen

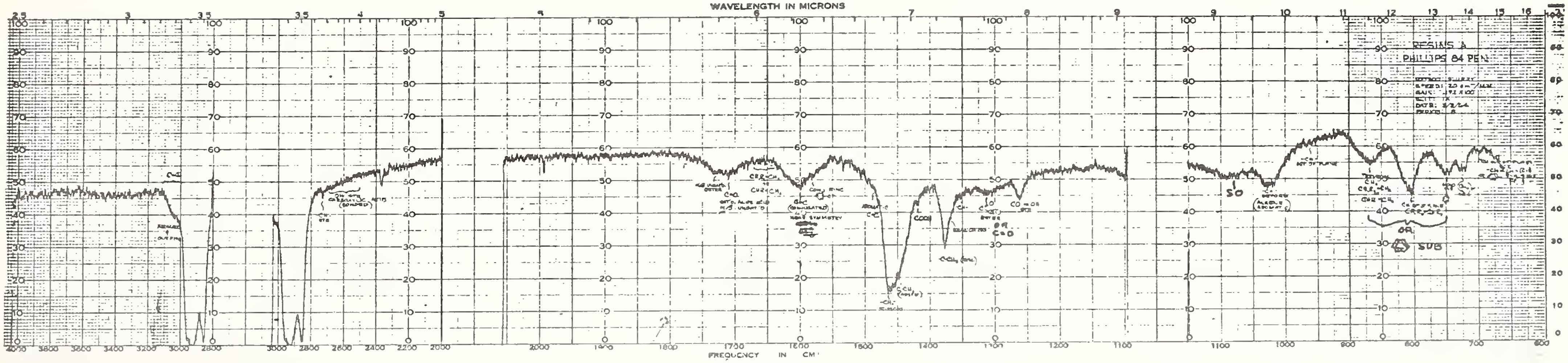


PLATE 5 Resin A Phillips 84 pen

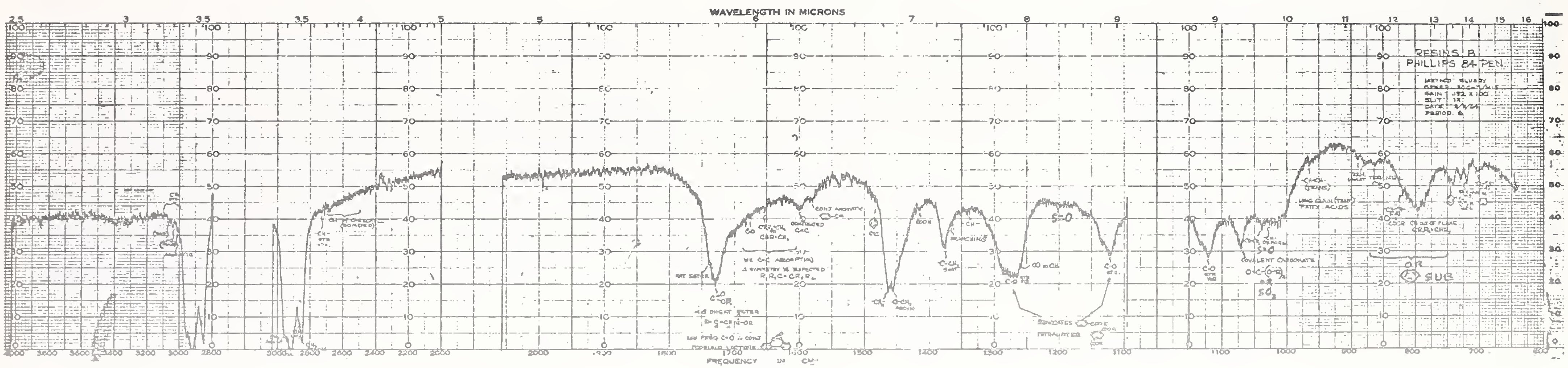


Plate 6 Resin B Phillips 84 pen

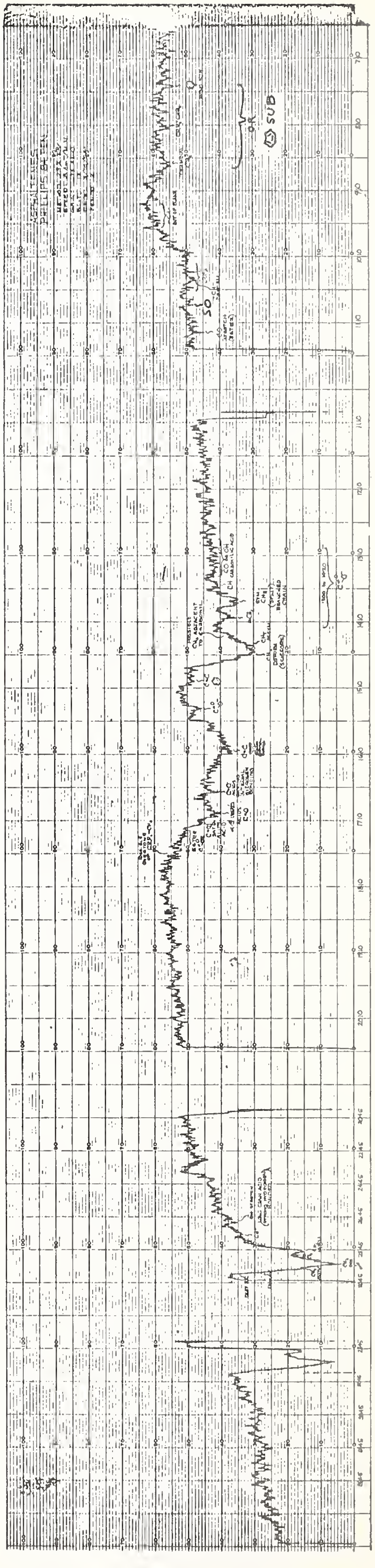


Plate 7 Asphaltines Phillips 84 pen

Spectral Analysis of Oils, Resins, Asphaltenes and Whole Asphalt

The discussion presented for the asphalt and its components has been based on a composite study of many spectra for each component. Individual samples of varying thicknesses were run for each infra-red order in order to present optimum absorption intensity and resolution for that wavenumber region. Charts reproduced here are of those samples which were run for the four orders and do not, therefore, represent the complete basis for the interpretive analysis.

1. Infra-red Spectra Analysis:

Whole Asphalt

3500 to 3200 cm^{-1} -- broad OH (associated) and perhaps NH.

3180 cm^{-1} -- NH_2

3100 to 2700 cm^{-1} -- CH_2, CH_3, and CH stretching frequencies.

2700 to 2500 cm^{-1} -- OH stretching frequency, strong hydrogen bonded as of carboxylic acids.

1800 to 1675 cm^{-1} -- C=O for saturated and unsaturated acids and for esters. Also, possible vinyl overtone.

1712 cm^{-1} -- C=O of unsaturated fatty acid. Peak may be intensified by addition of stearic acid, with no or little effect on other peaks in this range.

1650 cm^{-1} -- C=C, CR, $R_2=CH_2$, $CHR=CH_2$. Also, possible $CONH_2$; CO stretch for unsaturated aldehyde, ketone, or intra-molecularly bonded acid.

1600 cm^{-1} -- C=C (conjugated) Broadness of band due to mixture of conjugated and non-conjugated and for aromatic ring and straight chain. According to Bellamy (1), the

great majority of mono-substituted aromatics occur at 1600 ± 5 cm^{-1}. For para or tri-substituted materials, the shift is to higher frequencies.

1575 cm^{-1} -- A band in the 1587 to 1575 range is positive indication of conjugation of a double bond with an aromatic ring. In conjunction with a 1600 cm^{-1} absorption, it may be indicative of the benzoyl group, (1).

1500 cm^{-1} -- C=C, aromatic.

1460 cm^{-1} -- CH_2 and CH_3, deformation frequencies.

1375 cm^{-1} -- CH_3 symmetrical and branching indications.

1300 cm^{-1} -- SO_2 for Sulfones, CO or OH stretch of carboxylic acid. Also, possible CH_2 wag of paraffinic chain or aromatic aldehyde.

1170 cm^{-1} -- ester of carboxylic acid or dialkyl ester of sulfinic acid or NH stretch.

1130 cm^{-1} -- CO or SO stretch for ester.

1030 cm^{-1} -- CH out of plane stretch for aromatic ring or CH=CH-(trans). According to Stewart (2), the 1030 cm^{-1} peak may be oxygen, nitrogen or sulfur linkage. Schweyer (3), suggests its possibility as C-O, S=O, and Si-O absorption. However, it has been noted that those standard spectra for unsaturates of either olefinic (trans) or aromatic nature indicate a sharp, narrow band at 1030 cm^{-1}. The narrowness of the band as found in asphalt tends to indicate a CH stretching absorption rather than oxygen linkage since most oxygen linkages

are of a broader and more shallow character. Further, upon the addition of benzene to asphalt, the 1030 cm^{-1} spectral absorption was greatly intensified.

1090 to 1050 cm^{-1} -- S=O for sulphoxides, SO_2 for sulphones, sulfinic acid, and sulfonic acid. Also, possible covalent carbonate such as $=C-(O-R)_2$.

960 cm^{-1} -- CH out of plane for -CH=CH- (trans) or aromatic ring.

865 cm^{-1} -- 1,3,5 substitution of aromatic or terminal CH_2 for $R,R_2C=CH_2$ where frequency is lowered by two radicals, or for vinyl esters. Vinyl compounds of this type experience lower frequencies than literature cited for solid phase, certain substitutions, or for direct attachment of oxygen.

810 cm^{-1} -- 1,3 and 1,2,3 substitution of aromatic. Also, $CRR_2=CHR_3$ and -CH=CH-COOR.

745 cm^{-1} -- Mono or 1,2 disubstitution of aromatic.

720 cm^{-1} -- $(CH_2)_n$ chain vibration where n equals or is greater than 4.

700 cm^{-1} -- Mono or 1,3 disubstitution. Also, CH out of plane for -CH=CH-(Cis).

<u>Oils</u>

Aromatic and olefinic absorption is greatly diminished. There is minor indication of acid as in the whole asphalt. The oil fraction appears to be predominantly saturated aliphatic. The degree of branching tends to be higher in the oils than in any other fraction as

indicated by the 1315 cm^{-1} absorption and by the CH_2:CH_3 absorption ratio. There appear to be five methylene groups to every two methyl groups, or a carbon to hydrogen ratio of seven to sixteen.

Resins A

Intensity of aromatic and olefinic absorptions has increased greatly from that of oils, and from proportionate comparisons to CH_2 and CH_3 stretching, it indicates an almost equivalent unsaturation to that found in the whole asphalt. The formation of a broad band from 1700 to 1735 cm^{-1} and a band at 1260 cm^{-1} in addition to a series of weak bands from 1100 to 1325 cm^{-1} indicates the presence of acid and/or ester. In the solid state, the acid frequencies tend to be lowered; therefore, the high frequency C=O stretching vibration shows characteristics of ester in addition to acid. The peaks at 1125 cm^{-1} and 1265 cm^{-1} are characteristic absorptions for C-O- stretching vibrations of benzoates and phthalates. The greatly increased intensity of the 805 cm^{-1} might well support the presence of ester for the structure -CH=CH-COOR. Further, it helps to indicate the presence of olefinic as well as aromatic absorptions in the 750 to 900 cm^{-1} region.

Resins B

Intensity of CH_2 and CH_3 absorption is approximately equivalent to that of the whole asphalt, indicating seven methylene groups for every two methyl groups. There is evidently less branching and/or increased aromaticity as compared to Resins A. The major C=O stretch occurring at 1730 cm^{-1} is greatly enhanced along with other CO stretches

at 1275 cm^{-1} and 1125 cm^{-1}. Also, the proposed S=O absorption at 1040 cm^{-1} and at 1200 cm^{-1} for dialkyl sulphites is greater than that for other asphalt fractions. In addition the following possible sulfur linkages are noted: 1160 cm^{-1} -- aromatic $-SO_2-$, RO-SO-OR; 1135 cm^{-1} -- RSOOR; 1070 cm^{-1} -- RSOOH, ROSOOH ROSOR (also covalent carbonate, $O=C-(O-R)_2$). Both acids and esters of sulfur compounds appear to be present.

Once again, in conjunction with an apparent high concentration of ester, the 800 cm^{-1} peak is greatly intensified. Since this peak may represent 1,3 disubstituted and/or 1,2,3 tri-substituted aromatic or represent an ester of the form -CH=CH-COOR, the latter appears to be the favored assignment on the basis of ester concentration in Resin B. Whether the occurrence of ester may be attributed to its concentrated composition in Resin or its formation during solvent separation has not been ascertained. However, the great absorption intensities in Resin B, such as those at 1730, 1275, and 1125 cm^{-1} would be expected to indicate more prominent peaks in whole asphalt had they been caused by an initial component. Secondly, the evidence pointing toward a benzoate, phthalate, or lactone structure makes the benzene used in the solvent extraction suspect in the ester formation.

Asphaltenes

Asphaltenes exhibit a high CH_2 absorption as compared to CH_3, accounting for approximately seven methylene groups to each methyl group. The spectra revealed unsaturated structure, a fairly high concentration of CO, C=O, and OH groups, and little or no ester indication. The presence of OH groups was determined from a slurry

ANALYSIS OF ASPHALT COMPONENTS

Volatiles

Phillips 84 Penetration Asphalt was placed in a double-necked distillation flask and heated from 130° F to 300° F. Glass wool was used to hold a small amount (.75 to 1.0 gram) of powdered KBr in the neck of the drying tube. A vacuum connected to the drying tube raised the vapors from the heating asphalt in order to contaminate the KBr.

At every 10° temperature interval of the vapor, the KBr contaminated sample was removed and replaced by a pure KBr sample. A pellet was then made from the contaminated KBr.

This process was intended to show, by infra-red analysis, the lighter or more volatile components of asphalt.

Asphalt Unsaturation Determination

In the reaction of an alkene with a halogen, a di-halo alkene is produced without hydrohalide formation. The addition of bromine to a double bond yields a "Vic-dibromide" and is a standard test for unsaturation. The reaction is performed in a solution of carbon tetrachloride or chloroform and the discoloration of the bromine color indicates a positive test for unsaturation. While carbon tetrachloride is an ideal solvent for asphalt, the color change cannot be observed due to the presence of asphalt in the carbon tetrachloride solution. Because of the easy recovery of asphalt by evaporation of the carbon tetrachloride, the asphalt may be examined in the infra-red.

Asphalt has exhibited an infra-red peak at 1030 cm^{-1}, which may be assigned to the CH stretch. The assignment is apparently valid for either or both aliphatic and aromatic compounds, while the bromination reaction is only valid for aliphatic compounds; thus bromination followed by infra-red analysis should be able to indicate whether the 1030 cm^{-1} absorption peak is

due to aromatic or aliphatic compounds in the asphalt. Further, the peaks at 860, 810, 750, and 695 cm^{-1}, which have been attributed to substituted aromatic compounds may also be the assignment for alkene structures; therefore study of this region is in order. Although extensive side reactions were anticipated, these were not expected to interfere with the bands to be studied. The reaction for the bromination is:

$$R_1 \text{-}\overset{H}{C}=\overset{H}{C}\text{-}R_2 \quad + \quad 2Br \xrightarrow{U.V.} R_1\ \overset{H}{\underset{Br}{C}}\text{-}\overset{H}{\underset{Br}{C}}\text{-}R_2$$

Asphalt was dissolved in carbon tetrachloride and liquid bromine was added. The mixture was placed under an ultra-violet source for 24 hours. After the asphalt was recovered by volitizing the carbon tetrachloride solvent, the sample was analyzed with the infra-red. This analysis was inconclusive as many side reactions did seem in evidence.

<u>Esterification</u>

In theory, organic acids react with alcohols to form esters and water. A small amount of H_2SO_4 serves as a catalyst and a dehydrating agent, shortening the time of the reaction and giving better yields. The reaction is readily reversible in a basic solution.

$$R\text{-}C\begin{matrix} \diagup\!\!\!\!\diagup O \\ \diagdown OH \end{matrix} \quad + \quad HO\text{-}R \rightleftharpoons R\text{-}C\begin{matrix} \diagup\!\!\!\!\diagup O \\ \diagdown O\text{-}R \end{matrix} \quad + HOH$$

In the case of asphalt, the presence of acid should be demonstrated by a shift in the infra-red adsorption peaks and the production of intensification of an ester peak upon the addition of an excess of an alcohol. The addition of a base to the fractions of asphalt showing the ester peak should reverse the reaction and reproduce the acid.

Attempts have been made to prepare organic esters from the acid present in asphalt, using a mercurous nitrate catalyst, sulfuric acid as a dehydrating agent, and ethyl alcohol.

Since asphalt is predominately insoluble in alcohol, the reaction was performed in a carbon tetrachloride media. There had been no indication that carbon tetrachloride reacts with the constituents of asphalt.

Analysis by infra-red showed that sulfate esters and SO linkages of various types were formed. Attempts to recover the asphalt by an aqueous extraction of the alcohol and acid and subsequent evaporation of the carbon tetrachloride resulted in the formation of a black solid having the appearance of coal. Because of this, the extent of esterification of the acid originally present in asphalt is not known. It is felt that attempts to convert the asphalt acid into esters by slight variation of the standard reaction should be explored before attempting other methods. As such, the reaction, without the use of sulfuric acid should be performed. It is hoped that this will eliminate the SO linkages and probably allow the recovery of asphalt.

In the presence of suitable catalysts, unsaturated hydrocarbons undergo direct addition to organic acids. Mercurous ions in an acid medium catalize the vinyl acetate reaction.

$$CH_3 - C(=O)OH \quad + \quad H - C \quad C - H \longrightarrow CH_3 - C(=O) - O - CH = CH - H$$

The reaction of unsaturated hydrocarbons and organic acids will allow investigation into the possibility of a catalyst being present in fuller's earth. For use in column separation, fuller's earth is currently being employed. This reaction may be performed using fuller's earth, magnesium, calcium, and mercurous compounds, as possible catalysts.

CH_2:CH_3 Proportions in Asphalt

A study of the CH stretching mode absorptions for CH_3 at 2962 and 2872 cm^{-1} and for CH_2 at 2926 and 2853 cm^{-1} and of the CH deformation modes from 1340 to 1450 cm^{-1} allowed an approximation proportion of CH_3 and CH_2 to be calculated.

The intensities for known hydrocarbon absorptions of the CH stretching and deformation modes was correlated with the quantitative CH_3 and CH_2 proportions for the molecule (Table I). A plot of these values, absorption ratio versus quantity ratio, provided the curve in graph I. From this curve and the CH_3:CH_2 absorption ratio of the asphalt and its components, the CH_2:CH_3 proportion for the molecular structure was determined.

In order to establish the validity of this procedure, the values were tested in an equation whereby the sum of the asphalt component intensities should equal the intensity of the whole asphalt. Thus, the absorption intensity ratios for the parts were each evaluated on the basis of their fractional existence in asphalt and equated to the absorption intensity for the whole asphalt. Then:

$$A_oC_o + A_rC_r + A_aC_a = A_{wa}C_{wa}$$

Where: Absorption Ratio	Concentration
A_o (Oils) = .84	C_o (Oils) = 44%
A_r (Resins) = .68	C_r (Resins) = 34%
A_a (Asphaltenes) = .50	C_a (Asphaltenes) = 22%
A_{wa} (Whole Asphalt) = .71	C_{wa} (Whole Asphalt) = 100%

Therefore: $.84\ (.44) + .68\ (.34) + .50\ (.22) = .71\ (1.00)$

$$.7108 = .71$$

Absorption Ratio CH_3:CH_2 by Summation of Parts = Absorption Ratio of Whole Asphalt

The results indicate good agreement for the values obtained and a seemingly valid method and results for CH_2:CH_3 proportions determinations in asphalt.

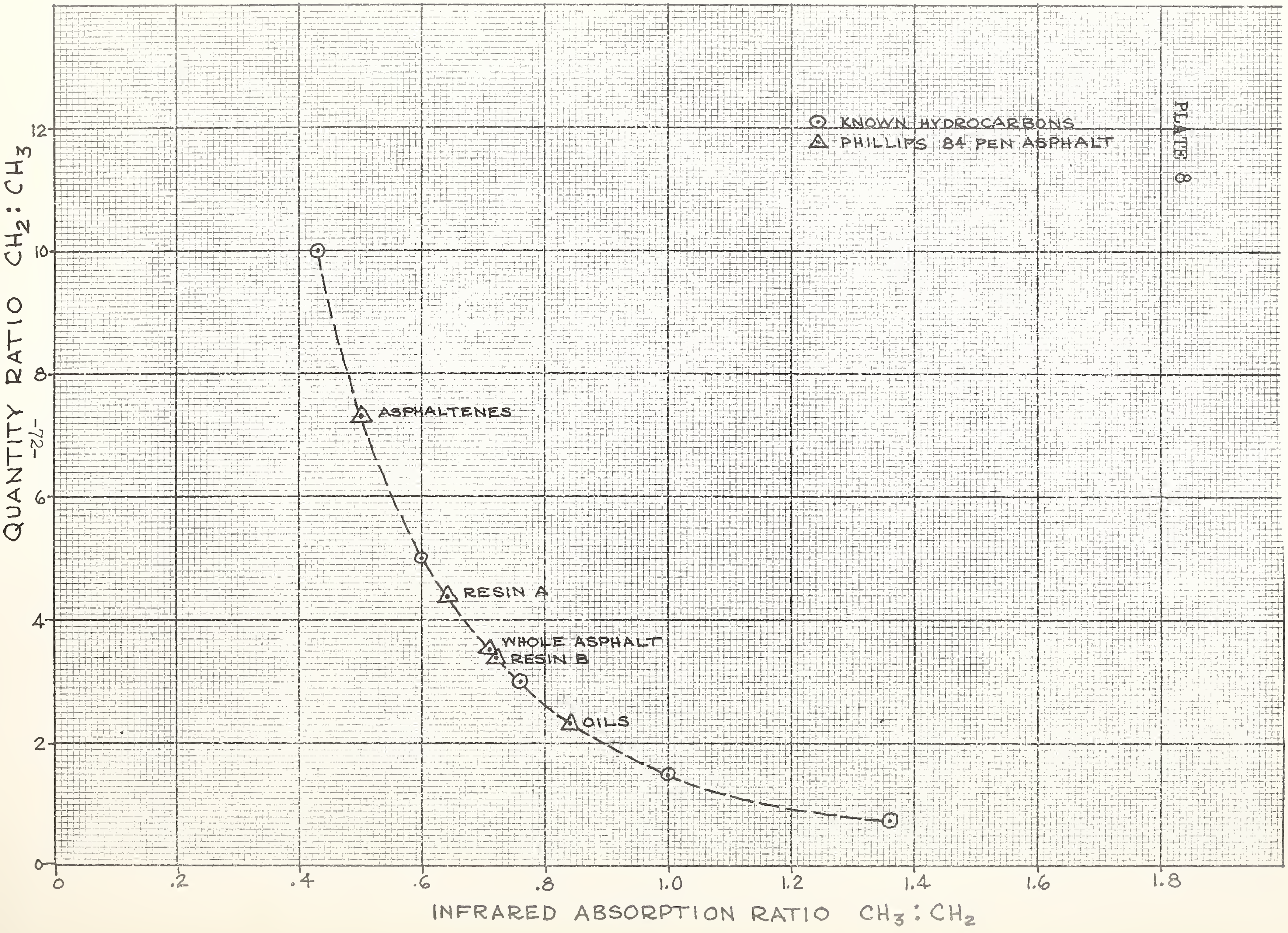


PLATE 8
⊙ KNOWN HYDROCARBONS
△ PHILLIPS 84 PEN ASPHALT
ASPHALTENES
RESIN A
WHOLE ASPHALT
RESIN B
OILS
QUANTITY RATIO $CH_2:CH_3$
INFRARED ABSORPTION RATIO $CH_3:CH_2$
0
2
4
6
8
10
12
0
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8

In agreement with other infra-red analysis of asphalts (2), the carbon to hydrogen ratio decreases in the following order: asphaltenes, resins, and oils.

Acid Components

From rough calculation in the application of Beer's Law, the carbonyl concentration in the whole asphalt sampled is estimated at two to four percent. That for the resin fraction is estimated at ten to fifteen percent. Since the resins comprise approximately one-third of the total asphalt, the major fraction of carbonyl groups appear to be isolated in the resins.

In the whole asphalt, the greatest carbonyl absorption intensity occurs at 1712 cm^{-1}. A summation of carbonyl intensities in the asphalt fractions shows the greatest carbonyl absorption at 1730 cm^{-1}. The disagreement can only be explained at this time on the basis of ester formation within the resins upon separation. Further, the 1275 cm^{-1} ester peak found in resins as a strong absorption does not appear as even a weak absorption in the whole asphalt. Thus, there appears to be sufficient evidence to indicate the esterification of acids in resins during the asphalt separation process. If this formation is assumed, the major portion of carbonyl absorption in asphalt may be attributed to carboxylic acid.

Unsaturated hydrocarbons will add directly to a carboxylic acid and produce an ester (5). In the presence of acid medium and a special catalyst, this addition process is favored. However, the catalyst effects only the rate of reaction. One such reaction of great importance to the plastic industry is the addition of acetylene to acetic acid to produce vinyl acetate:

$$CH_3 - \overset{O}{C} - OH + HC{=}CH \xrightarrow[H^+]{Hg^{++}} CH_3\text{-}C\text{-}O\text{-}C{=}CH_2$$

Since the major constituents of fuller's earth are attapulgite, $(OH_2)_4(OH)_2\ Mg_5Si_8O_{20}.4H_2O$, and montmorillonite, $(Mg,Ca)\ O.Al_2O_3.5SiO_3.nH_2O$, it is possible that the soft metals may have a catalytic effect on the addition of unsaturates to acids during resin fraction removal.

TABLE I

KNOWN HYDROCARBONS

Compound	I.R. Absorption Ratio $CH_3:CH_2$	Quantity Ratio $CH_2:CH_3$
Naphtha Approx. (C_4 to C_7)	1.00	3:2
Dodecane $CH_3(CH_2)_{10}CH_3$	.60	5:1
Docosane $CH_3(CH_2)_{20}CH_3$	.43	10:1
Vaseline Approx. (C_{25} to C_{30})	.76	3:1
N-Pentane $CH_3(CH_2)_3CH_3$	1.00	3:2
Kerosene Approx. (C_8 to C_{17})	.76	3:1
3 Ethyl 3 Methyl Pentane $CH_3CH_2C(CH_3)(C_2H_5)CH_2CH_3$	1.36	3:4

PHILLIPS 84 PEN ASPHALT: Solvent Extraction & Absorption Method of Separation (Marcusson Method)

Asphalt Component	I.R. Absorption Ratio $CH_3:CH_2$		Quantity Ratio $CH_2:CH_3$	% Conc. in Asphalt
Oils	.84		2.3:1	44%
Resins A	.64	.68 avg.	4.4:1	34%
Resins B	.72		3.4:1	
Asphaltenes	.50		7.3:1	22%
Whole Asphalt	.71		3.5:1	100%

PART I-C

A STUDY OF THE TRAXLER-SCHWEYER SEPARATION METHOD

The work done on the $CH_3 | CH_2$ ratio suggests a method for evaluating the various solvent separation techniques. This has been done in the case of the Traxler method by using a number of different asphalts.

Separation Procedure

1. Asphaltenes

   Removed with n-pentane and dried to constant weight.

2. Asphaltics

   Insoluble in n-butanol.

3. Cyclics

   Soluble in n-pentane and acetone; recovered by evaporation of solvents.

4. Petrolenes

   Treated with dried fuller's earth and extracted with n-pentane.

5. Saturates

   Soluble in n-pentane and precipitated with acetone.

Absorption Ratio Method

Beer's law states that the absorbancy (A) is proportional to the cell thickness (B) times the concentration (C). The proportionality constant is termed the extinction co-efficient.

$$A = KCB$$

For any separation, the whole should equal the sum of the parts, so for this system:

$$A_{\text{whole asphalt}} = A_{\text{cyclics}} + A_{\text{asphaltics}} + A_{\text{petrolenes}} + A_{\text{saturates}}$$

From Beer's law applied to the CH_3 wavelength (2872)

$$(K_{CH_3}\ B\ C_{CH_3})\ \text{whole} = (K_{CH_3}\ B\ C_{CH_3})\ \text{cy} + \ldots$$

The value of the constant B can be obtained by using a different absorption peak. Take the CH_2 peak (2853).

$$B = \frac{A_{CH_2}}{K_{CH_2}\ C_{CH_2}}$$

Whence:

$$\left(\frac{K_{CH_3}\ A_{CH_2}\ C_{CH_3}}{K_{CH_2}\ C_{CH_2}}\right)\ \text{whole} = \left(\frac{K_{CH_3}\ C_{CH_3}\ A_{CH_2}}{K_{CH_2}\ C_{CH_2}}\right)\ \text{cyclics} + \ldots.$$

or:

$$\left(\frac{A_{CH_3}}{A_{CH_2}}\right)\ \text{whole} = \frac{(A_{CH_2})\ \text{cy}}{(A_{CH_2})W} \times \frac{(A_{CH_3})\ \text{cy}}{A_{CH_2}} + \frac{(A_{CH_2})\text{as}}{(A_{CH_3})W} \times \frac{(A_{CH_3})\ \text{as}}{A_{CH_2}} + \ldots$$

The coefficients of the ratios are simply the fractional part that each component is of the whole asphalt. The absorption ratio of the whole asphalt must equal the sum of the absorption ratios of each component times its fractional part.

If any chemical reaction or change occurs during the separation process, the groups effected will be obvious as their ratios will not obey the above rule. A larger number on the component side indicates that material was in-

corporated from the solvent or from another functional group. Reactants should yield a deficiency while products will give a positive number.

Sample Preparation

Preparing samples made from Diamond 107 Pen asphalt proved to be a difficult task. This type of asphalt is very thick and hard to use. A small amount of specimen is placed on an NaCl plate, and a glass stirring rod is employed to roll the sample to desired thickness, being cleaned with CCl_4 between each rolling, until desired thickness of sample is reached. Sometimes the glass stirring rod had to be slightly heated to facilitate the process.

The cyclics prepared for testing can easily be made into thin film for analyzing on the IR-7. Preparation of the asphaltenes present no special problems, strictly routine KBr pellets plus the asphaltene.

When working with the esters, which were obtained from the distillation of Diamond 107 Pen, it was found necessary to dissolve them in CCl_4. For this type of specimen, no spacer was found to be necessary between the NaCl plates.

The petrolenes must be heated to be able to obtain a reasonably soft consistency for preparing a slurry type sample.

The oils which are obtained from the esters of Diamond 107 Pen, present somewhat of a different problem. As it is generally known, the oils will form on the top of the water residue left from the distillation. These droplets must be removed very carefully so as not to collect an undue amount of H_2O, which would be ruinous to the NaCl plates. The sample can be dissolved in CCl_4 and then processed in the same manner as the ester formation.

Discussion

In computing the absorption ratio, the CH_2 band at 2853 cm^{-1} was used. It has been previously established that the sum of the absorption ratio times the concentrations of the components at this wave number gives results which more nearly equal the ratio of the whole asphalt than do other bands.

In Table IV the tabulated column, Summation - AwCw, shows the difference between the sum and the total. If the sign of the tabulated value is positive, it is an indication that this material was produced in the extraction process by some reaction. As is noted, there is a decrease in the 1(H), and 2(H), and 3(H), while an increase in the $C-(CH_3)n$ and $C-CH_3$. This may be an indication that the latter are being formed at the expense of the former. The sum of the numerical values in this column is ± 1.114. This is an indication that some of the solvents are undergoing additional reactions during the extraction.

Table VII is a tabulation of the absorption ratio multiplied by the concentration of the fraction. It was thought that this tabulation might indicate where the functional groups were being distributed in the extraction.

For the $(CH_2)n$ ratio one would expect the majority of the material to be found in the saturates. As expected, the saturates appear to contain 50% of this material. Another interesting aspect is that most of the sulphur containing groups appear in the petrolenes. The C=C aromatic, C=C aliphatic, C=O at 1700 cm^{-1}, and the C=O at 1760 cm^{-1} seem to be in disagreement. The possibility exists that discrepancies may be accounted for by other groups absorbing at these frequencies and intensifying these regions. For example, if an aromatic ring possesses a long saturated side chain, the molecule may be carried into the saturates, thus producing a high C=C aromatic absorption. This may account for the 35% value in the saturates for the C=C aromatic.

TABLE I

FARMERS - 96 PEN ASPHALT SUMMATIONS

	1	2	3	4	5	6	7
5H	.018	.017	.030	.023	.088	.088	0
$(CH_2)n$	.028	.036	.045	.109	.412	.218	-.194
4 or 5 (H)	.043	.053	.037	.068	.427	.201	-.226
4 or 5 (H)	.105	.046	.030	.050	.382	.231	-.151
3 (H) adj.	.145	.031	.030	.036	.294	.242	-.052
2 (H) adj.	.028	.053	.030	.055	.455	.166	-.289
1 (H)	.022	.038	.022	.046	.427	.128	-.299
S=O or R-S-R	.022	.036	.075	.041	.162	.174	+.012
CH (arom)	.022	.038	.060	.050	.235	.170	-.065
SO_3H or -S-R	.015	.026	.045	.036	.191	.122	-.069
SO_2 ester	.043	.065	.158	.096	.073	.362	+.289
ester	.040	.065	.112	.105	.103	.322	+.219
CO or OH or SO_2	.040	.094	.060	.137	.147	.331	+.184
C- $(CH_3)n$	.053	.103	.097	.214	.235	.467	+.232
C-CH_3	.074	.137	.150	.301	.382	.662	+.280
CH_2	.108	.173	.248	.374	.602	.903	+.301
C=C arom	.046	.079	.053	.096	.132	.274	+.142
C=C olefin	.022	.048	.022	.055	.073	.147	+.057
C=O	.012	.048	.022	.055	.044	.137	+.093
C=O	.006	.022	.030	.014	.015	.072	+.057
CH	.155	.012	.030	.014	.073	.211	+.138
CH_2	.170	.120	.450	.260	1.000	1.000	0
CH_3	.142	.113	.383	.192	.838	.830	-.008
CH_2	.229	.163	.585	.347	1.235	1.324	+.089
CH_3	.173	.142	.450	.246	.986	1.011	+.025
CH_2	.164	.450	.435	.251	.971	1.300	+.329
CH_3	.136	.113	.353	.192	.868	.794	-.074
CH_2	.223	.163	.577	.337	1.205	1.300	+.095
CH_3	.167	.142	.443	.237	.971	.989	+.018
≡C-H	.025	.019	.030	.018	.118	.092	-.026
OH	.009	.007	.015	.005	.044	.036	-.008

Legend for Numbered Columns
No. 1: .17, AaCa
No. 2: .12, AcCc
No. 3: .45, ApCp
No. 4: .26, AsCs
No. 5: AwCw
No. 6: Summation of AaCa+AcCc+ApCp+AsCs
No. 7: Summation Minus AwCw

TABLE II

FARMERS - 100-120 PEN ASPHALT SUMMATION

	1	2	3	4	5	6	7
5H	.016	.022		.058	.048	.096	+.048
$(CH_2)n$	.028	.078		.214	.371	.320	-.051
4 or 5 (H)	.033	.117		.148	.371	.298	-.073
4 or 5 (H)	.039	.109		.123	.339	.271	-.068
3 (H) adj.	.039	.078		.082	.242	.199	-.043
2 (H) adj.	.033	.126		.132	.403	.291	-.112
1 (H)	.039	.091		.115	.355	.245	-.110
S=O or R-S-R	.033	.095		.115	.113	.243	+.130
CH (arom)	.039	.100		.132	.161	.271	+.110
SO_3H or -S-R	.033	.056		.082	.129	.171	+.042
SO_2 ester	.028	.148		.271	.435	.447	+.012
ester	.044	.165		.288	.516	.497	-.019
CO or OH or SO_2	.060	.204		.354	.694	.618	-.076
C- $(CH_3)n$	.088	.252		.494	.935	.834	-.101
$C-CH_3$	.121	.304		.600	1.117	1.025	-.152
CH_2	.171	.357		.666	1.371	1.194	-.177
C=C arom	.072	.204		.304	.629	.580	-.049
C=C olefin	.033	.121		.173	.323	.327	+.004
C=O	.033	.135		.197	.162	.365	+.203
C=O	.011	.095		.058	.081	.164	+.083
CH	.022	.022		.033	.081	.077	-.004
CH_2	.270	.230		.510	1.000	1.010	+.010
CH_3	.221	.217		.387	.855	.826	-.022
CH_2	.347	.308		.658	1.194	1.313	+.119
CH_3	.270	.265		.494	.984	1.029	+.045
CH_2	.242	.221		.502	.952	.967	+.015
CH_3	.193	.208		.403	.823	.804	-.019
CH_2	.314	.304		.642	1.177	1.260	+.083
CH_3	.242	.260		.486	.984	.988	+.004
=C-H	.028	.043		.041	.129	.112	-.017
OH	.011	.026		.016	.048	.053	+.005
	+4	+3		+21	+8		
	-4	-5			-1	Total	-.180

Legend for Numbered Columns
No. 1: .27, AaCa
No. 2: .23, AcCc
No. 3: ApCp
No. 4: .51, AsCs
No. 5: AwCw
No. 6: Summation of AaCa+AcCc+ApCp+AsCs
No. 7: Summation Minus AwCw

TABLE III

PHILLIPS 100-120 PEN

	1	2	3	4	5	6	7
5H	.024	.021		.020	.083	.065	-.018
$(CH_2)n$	.053	.067		.192	.433	.312	-.121
4 or 5 (H)	.057	.105		.126	.433	.288	-.145
4 or 5 (H)	.053	.094		.099	.367	.246	-.121
3 (H) adj.	.043	.067		.066	.267	.176	-.091
2 (H) adj.	.057	.105		.106	.433	.268	-.165
3 (H)	.053	.074		.079	.367	.206	-.045
S=O or R-S-R	.038	.061		.073	.217	.172	-.057
CH (arom)	.043	.074		.093	.267	.210	-.061
SO_3H or ⌬-S-R	.034	.046		.059	.200	.139	-.160
SO_2 ester	.082	.116		.159	.517	.357	-.305
ester	.101	.127		.185	.617	.312	-.210
CO or OH or SO_2	.125	.154		.278	.767	.557	-.264
C- $(CH_3)n$	.153	.196		.404	1.017	.753	-.295
C-CH_3	.197	.242		.516	1.250	.955	-.202
CH_2	.283	.277		.655	1.417	1.215	-.228
C=C arom	.125	.151		.179	.683	.455	-.135
C=C olefin	.067	.088		.093	.383	.248	+.040
C=O	.053	.088		.099	.200	.240	+.072
C=O	.014	.035		.033	.010	.082	+.014
CH	.043	.021		.033	.083	.097	0.000
CH_2	.350	.200		.450	1.000	1.000	-.002
CH_3	.312	.189		.364	.867	.865	-.053
CH_2	.398	.253		.563	1.267	1.214	-.034
CH_3	.307	.225		.430	.996	.962	+.014
CH_2	.331	.196		.437	.783	.964	+.044
CH_3	.297	.179		.351	1.250	.827	-.077
CH_2	.384	.246		.543	.933	1.173	+.033
CH_3	.331	.218		.417	.117	.966	+.027
=C-H	.072	.039		.033	.033	.144	+.022
OH	.024	.018		.013		.055	

Total -2.684

Legend for Numbered Columns

No. 1: .35, AaCa

No. 2: .20, AcCc

No. 3: ApCp

No. 4: .45, AsCs

No. 5: AwCw

No. 6: Summation of AaCa+AcCc+ApCp AsCs

No. 7: Summation Minus AwCw

TABLE IV

HUMBLE 100-120 PEN

	1	2	3	4	5	6	7
5H	.018	.020		.036	.059	.074	+.015
$(CH_2)n$	.084	.041		.173	.382	.298	-.084
4 or 5 (H)	.101	.075		.116	.400	.292	-.108
4 or 5 (H)	.089	.064		.087	.364	.240	-.124
3 (H) adj.	.066	.048		.058	.254	.172	-.082
2 (H) adj.	.113	.078		.101	.436	.292	-.144
1 (H)	.107	.058		.079	.382	.244	-.138
S=O or R-$\overset{O}{\overset{\|}{S}}$-R	.066	.058		.079	.218	.203	-.015
CH (arom)	.084	.064		.094	.236	.242	+.006
SO_3H or $\bigcirc$-$\overset{O}{\overset{\|}{S}}$-R	.048	.034		.058	.164	.140	-.024
SO_2 ester	.155	.085		.159	.473	.399	-.074
ester	.185	.095		.188	.564	.468	-.096
CO or OH or SO_2	.233	.122		.246	.764	.601	-.163
C- $(CH_3)n$	.274	.149		.383	1.054	.806	-.248
C-CH_3	.334	.200		.513	1.309	1.047	-.262
C=C arom	.394	.244		.593	1.527	1.231	-.296
C=C olefin	.233	.119		.188	.673	.540	-.133
C=O	.119	.075		.109	.327	.303	-.024
C=O	.107	.075		.123	.164	.305	+.141
CH	.036	.027		.036	.091	.099	+.008
CH_2	.048	.017		.029	.091	.094	+.003
CH_3	.340	.190		.470	1.000	1.000	+.000
CH_2	.298	.183		.391	.800	.872	+.072
CH_3	.411	.261		.586	1.309	1.258	-.051
CH_2	.340	.193		.463	1.018	1.030	+.012
CH_3	.316	.180		.463	.964	.972	+.008
CH_2	.286	.261		.391	.782	.857	+.075
CH_3	.406	.227		.593	1.254	1.260	+.006
=C-H	.322	.044		.455	.945	1.004	+.059
OH	.089	.024		.029	.091	.162	+.071
	.030			.015	.036	.069	+.033
						Total	-1.557

Legend for Numbered Columns
No. 1: .34, AaCa
No. 2: .19, AcCc
No. 3: ApCp
No. 4: .47, AsCs
No. 5: AwCw
No. 6: Summation for AaCa+AcCc+ApCp+AsCs
No. 7: Summation Minus AwCw

TABLE V

DIAMOND 100-120 PEN

	1	2	3	4	5	6	7
5H	.028	.022		.021	.066	.071	+.005
$(CH_2)n$	.039	.084		.218	.410	.341	-.069
4 or 5 (H)	.045	.124		.133	.410	.302	-.108
4 or 5 (H)	.033	.101		.105	.377	.239	-.138
3(H) ADJ	.028	.070		.077	.262	.175	-.087
2(H) ADJ	.039	.115		.105	.393	.259	-.134
1(H)	.033	.070		.070	.311	.173	-.138
S=O or R-S-R	.033	.084		.098	.197	.215	+.018
CH (arom)	.039	.093		.105	.230	.237	+.007
SO_3H or ⌬-S-R	.028	.044		.070	.164	.142	-.022
SO_2 Ester	.045	.037		.204	.541	.286	-.255
Ester	.061	.150		:232	.639	.443	-.196
CO, OH, or SO_2	.078	.181		.288	.803	.547	-.256
$C-(CH_3)n$	.095	.238		.407	1.000	.740	-.260
$C-CH_3$	.128	.308		.519	1.213	.955	-.258
C=C arom	.195	.370		.624	1.377	1.189	-.188
C=C olefin	.084	.159		.204	.738	.447	-.291
C=O	.056	.106		.154	.492	.316	-.176
C=O	.033	.101		.119	.230	.253	+.023
CH	.011	.044		.035	.115	.090	-.025
CH_2	.033	.022		.028	.082	.083	+.001
CH_3	.340	.260		.400	1.000	1.000	.000
CH_2	.256	.242		.309	.803	.807	+.004
CH_3	.412	.348		.540	1.295	1.300	+.005
CH_2	.312	.300		.372	.984	.984	.000
CH_3	.284	.260		.386	.951	.930	-.021
CH_2	.223	.242		.288	.770	.753	-.017
CH_3	.373	.348		.526	1.262	1.247	-.014
=C-H	.279	.300		.358	.951	.937	-.026
OH	.028	.040		.021	.115	.089	+.004
	.017	.022		.014	.049	.053	
							-2.627

Legend for numbered columns

No. 1: 34 AaCa
2: 26 AcCc
3: ApCp
4: 40 AsCs
5: AwCw
6: AaCa+AcCc+ApCp+AsCs Summation
7: Summation - AwCw

TABLE VI

BIG WEST 100-120 PEN

	1	2	3	4	5	6	7
5H	.047	.088		.034	.164	.169	+.005
$(CH_2)n$	.040	.106		.172	.509	.318	-.191
4 or 5 (H)	.063	.372		.118	.727	.553	-.174
4 or 5 (H)	.071	.345		.103	.673	.519	-.154
3(H) ADJ	.071	.257		.079	.545	.407	-.138
2(H) ADJ	.071	.380		.118	.782	.569	-.213
1(H)	.071	.310		.098	.673	.479	-.194
S=O or R-S-R	.047	.150		.064	.255	.261	+.006
CH (arom)	.055	.203		.079	.382	.337	-.045
SO_3H or⬭-S-R	.040	.124		.064	.236	.228	-.008
SO_2 ester	.071	.389		.123	.582	.583	+.001
ester	.071	.354		.143	.636	.568	-.068
CO or OH or SO_2	.087	.433		.182	.855	.702	-.153
$C-(CH_3)n$	.102	.548		.255	1.036	.905	-.131
$C-CH_3$	.142	.646		.339	1.309	1.127	-.182
CH_2	.205	.743		.408	1.509	1.356	-.153
C=C arom	.102	.504		.167	.945	.773	-.172
C=C olefin	.047	.247		.088	.327	.382	+.055
C=O	.040	.389		.098	.255	.527	+.277
C=O	.024	.132		.034	.200	.190	-.010
CH	.024	.044		.020	.091	.088	-.003
CH_2	.260	.460		.280	1.000	1.000	-.000
CH_3	.229	.443		.197	.873	.869	-.004
CH_2	.418	.637		.368	1.182	1.423	+.241
CH_3	.284	.548		.241	1.018	1.073	-.055
CH_2	.252	.469		.275	1.000	.996	-.004
CH_3	.220	.443		.187	.873	.850	-.023
CH_2	.402	.646		.363	1.182	1.411	+.229
CH_3	.276	.548		.231	1.000	1.055	+.055
=C-H	.063	.142		.025	.255	.230	-.025
OH	.016	.044		.010	.055	.070	+.015

-1.216

Legend for numbered columns

No. 1: .17 AaCa
2: .12 AcCc
3: .45 ApCp
4: .26 AsCs
5: AwCw
6: AaCa+AcCc+ApCp+AsCs Summation
7: Summation - AwCw

TABLE VII

CONOCO 100-120 PEN

	1	2	3	4	5	6	7
5H	.027	.053		.012	.106	.092	-.014
$(CH_2)n$	.053	.165		.129	.489	.347	-.142
4 or 5 (H)	.073	.330		.081	.702	.487	-.215
4 or 5 (H)	.073	.307		.077	.660	.457	-.203
3 (H) ADJ	.047	.225		.073	.484	.345	-.144
2 (H) ADJ	.080	.353		.073	.787	.506	-.281
1 (H)	.080	.270		.060	.681	.410	-.271
S=O or R-S-R	.040	.165		.053	.383	.258	-.125
CH (arom)	.053	.202		.060	.489	.315	-.175
SO_3H or ⬭-S-R	.040	.120		.044	.319	.204	-.115
SO_2 Ester	.080	.248		.101	.638	.429	-.209
Ester	.100	.270		.117	.745	.487	-.258
CO, OH, or SO_2	.133	.337		.149	.979	.619	-.360
C- $(CH_3)n$	.167	.420		.223	1.234	.810	-.424
$C-CH_3$	.220	.548		.290	1.489	1.058	-.431
CH_2	.280	.622		.347	1.681	1.249	-.432
C=C arom	.147	.390		.125	1.043	.662	-.381
C=C olefin	.067	.225		.089	.596	.381	-.215
C=O	.047	.180		.069	.298	.296	-.002
C=O	.020	.090		.020	.170	.430	+.260
CH	.047	.045		.020	.128	.412	+.284
CH_2	.380	.390		.230	1.000	1.000	.000
CH_3	.347	.375		.178	.851	.900	+.049
CH_2	.473	.548		.307	1.277	1.328	+.051
CH_3	.400	.473		.214	1.043	1.087	+.044
CH_2	.347	.367		.214	.915	.928	+.013
CH_3	.307	.360		.157	.766	.824	+.058
CH_2	.447	.532		.290	1.214	1.269	+.056
CH_3	.367	.457		.202	.957	1.026	+.069
=C-H	.073	.120		.020	.149	.213	+.064
OH	.013	.023		.012	.064	.048	-.016

Legend for numbered columns

No. 1: .38 AaCa
2: .39 AcCc
3: ApCp
4: .23 AsCs
5: AwCw
6: AaCa+AcCc+ApCp+AsCs Summation
7: Summation AwCw

TABLE VIII

FARMERS - 96 PEN ASPHALT CONCENTRATION DISTRIBUTION

	ASPHALTINES %AaCa	CYCLICS %AcCc	PETROLENES %ApCp	SATURATES %AsCs
5H	21	19	34	26
$(CH_2)n$	13	16	21	50
4 or 5 (H)	21	27	18	34
4 or 5 (H)	45	20	13	22
3 (H) ADJ	60	13	12	15
2 (H) ADJ	17	32	18	33
1 (H)	17	30	17	36
S=O or R-S-R	13	21	43	23
CH (arom)	13	22	35	30
SO_3H or ⌬-S-R	12	21	37	30
SO_2 ester	12	18	44	26
ester	12	20	35	33
CO, OH, or SO_2	12	29	18	41
C- $(CH_3)n$	11	22	21	46
$C-CH_3$	11	21	23	45
CH_2	12	19	28	41
C=C (arom)	17	29	19	35
C=C (olefin)	15	33	15	37
C=O	9	35	16	40
C=O	8	31	42	19
CH	73	6	14	7
CH_2	17	12	45	26
CH_3	17	14	46	23
CH_2	17	13	44	26
CH_3	17	14	45	24
CH_2	13	35	33	19
CH_3	17	14	45	24
CH_2	17	13	44	26
CH_3	17	14	45	24
=C-H	27	21	33	19
OH	25	19	42	14

TABLE IX

FARMERS - 100-120 PEN ASPHALT CONCENTRATION DISTRIBUTION

	Asphaltines %AaCa	Cyclics %AcCc	Petrolenes %AsCs	Saturates %AwCw
5H	17	23	60	50
$(CH_2)n$	9	25	64	120
4 or 5 (H)	11	39	50	125
4 or 5 (H)	14	40	46	126
3 (H) ADJ	20	39	41	122
2 (H) ADJ	11	43	46	139
1 (H)	16	37	47	145
S=O or R-S-R	14	39	47	46
CH (arom)	14	37	49	60
SO_3H or -S-R	19	33	48	75
SO_2 ester	20	28	52	84
ester	9	33	58	104
CO, OH, or SO_2	10	33	57	112
C- $(CH_2)n$	10	30	60	112
$C-CH_3$	12	30	58	115
CH_2	14	30	56	111
C=C (arom)	12	35	53	109
C=C (olefin)	10	37	53	99
C=O	9	37	54	44
C=O	7	58	35	49
CH	29	29	42	105
CH_2	27	23	50	99
CH_3	26	26	48	103
CH_2	26	23	51	91
CH_3	26	26	48	96
CH_2	25	23	52	98
CH_3	24	26	50	102
CH_2	25	24	51	94
CH_3	25	26	49	99
=C-H	25	39	36	114
OH	21	49	30	90

TABLE X

FARMERS - 96 PEN (WHOLE ASPHALTS)

Group Freq.		Δ% T	X %T/CH_2 (%T @2853
First Order			
(5H)	700	6	.088
$(CH_2)n = 4$	720	28	.412
4 or 5(H)	750	29	.427
4 or 5(H)	760	26	.382
3(H) ADJ	785	20	.294
2(H) ADJ	810	31	.455
1(H) ADJ	870	29	.427
(S=O) R-S-R	1020	11	.162
CH (AROM)	1030	16	.235
(SO_3H) S-R	1060	13	.191
Second Order			
SO_2 Ester	1165	5	.073
Ester (SO_2)	1260	7	.103
CO, OH or SO_2	1300-1320	10	.147
$C-(CH_3)n$	1368	16	.235
$C-CH_3$	1380	26	.382
CH_2	1460	41	.602
C=C(AROM)	1600	9	.132
C=C(olefin) -	1660	5	.073
C=O	1700	3	.044
C=O	1760	1	.015
Third Order			
CH	2720	5	.073
CH_2	2853	68	1.000
CH_3	2872	57	.838
CH_2	2926	84	1.235
CH_3	2962	67	.986
Fourth Order			
CH_2	2853	66	.971
CH_3	2872	59	.868
CH_2	2926	82	1.205
CH_3	2962	66	.971
=C-H	3030	8	.118
OH	3300	3	.044

TABLE XI

FARMERS - 96 PEN ASPHALTICS

Group Freq.		Δ % T	X %T/CH_2 (%T @ 2853
First Order			
(5H)	700	6	.109
$(CH_2)n = 4$	720	9	.164
4 or 5(H)	750	14	.254
4 or 5(H)	760	34	.618
3(H) ADJ	785	47	.855
2(H) ADJ	810	9	.164
1(H) ADJ	870	7	.127
(S=O) R-S-R	1020	7	.127
CH (AROM)	1030	7	.127
(SO_3H) S-R	1060	5	.091
Second Order			
SO_2 Ester	1165	14	.254
Ester (SO_2)	1260	13	.236
CO, OH or SO_2	1300-1320	13	.236
C-$(CH_3)n$	1368	17	.309
C-CH_3	1380	24	.436
CH_2	1460	35	.637
C=C (AROM)	1600	15	.273
C=C (oleofin) -	1660	7	.127
C=O	1700	4	.073
C=O	1760	2	.036
Third Order			
CH	2720	5	.910
CH_2	2853	55	1.000
CH_3	2872	46	.837
CH_2	2926	74	1.345
CH_3	2962	56	1.020
Fourth Order			
CH_2	2853	53	.964
CH_3	2872	44	.800
CH_2	2926	72	1.310
CH_3	2962	54	.982
=C-H	3030	8	.145
OH	3300	3	.055

TABLE XII

FARMERS - 96 PEN CYCLICS

Group Freq.		Δ % T	X %T/CH_2 (%T @ 2853)
First Order			
(5H)	700	7	.140
$(CH_2)n = 4$	720	15	.300
4 or 5(H)	750	22	.440
4 or 5(H)	760	19	.380
3(H) ADJ	785	13	.260
2(H) ADJ	810	22	.440
1(H) ADJ	870	16	.320
(S=O) R-S-R	1020	15	.300
CH (AROM)	1030	16	.320
(SO_3H) -S-R	1060	11	.220
Second Order			
SO_2 Ester	1165	27	.540
Ester (SO_2)	1260	27	.540
CO, OH or SO_2	1300-1320	34	.780
C-$(CH_3)n$	1368	43	.860
C-CH_3	1380	57	1.140
CH_2	1460	72	1.440
C=C (AROM)	1600	33	.660
C=C(olefin) -	1660	20	.400
C=O	1700	20	.400
C=O	1760	9	.180
Third Order			
CH	2720	5	.100
CH_2	2853	50	1.000
CH_3	2872	47	.940
CH_2	2926	68	1.360
CH_3	2962	59	1.180
Fourth Order			
CH_2	2853	50	1.000
CH_3	2872	47	.940
CH_2	2926	68	1.360
CH_3	2962	59	1.180
=C-H	3030	8	.160
OH	3300	3	.060

TABLE XIII

FARMERS - 96 PEN PETROLENES

Group Freq.		Δ % T	X %T/CH_2 (%T @ 2853
First Order			
(5H)	700	4	.067
$(CH_2)n = 4$	720	6	.100
4 or 5(H)	750	5	.083
4 or 5(H)	760	4	.067
3(H) ADJ	785	4	.067
2(H) ADJ	810	4	.067
1(H) ADJ	870	3	.050
(S=O) R-S-R	1020	10	.167
CH (AROM)	1030	8	.134
(SO_3H) S-R	1060	6	.100
Second Order			
SO_2 Ester	1165	21	.350
Ester (SO_2)	1260	15	.250
CO, OH or SO_2	1300-1320	8	.134
$C-(CH_3)n$	1368	13	.216
$C-CH_3$	1380	20	.333
CH_2	1460	33	.550
C=C (AROM)	1600	7	.117
C=C(olefin) -	1660	3	.050
C=O	1700	3	.050
C=O	1760	4	.067
Third Order			
CH	2720	4	.067
CH_2	2853	60	1.000
CH_3	2872	51	.851
CH_2	2926	78	1.300
CH_3	2962	60	1.000
Fourth Order			
CH_2	2853	58	.966
CH_3	2872	47	.783
CH_2	2926	77	1.283
CH_3	2962	59	.984
=C-H	3030	4	.067
OH	3300	2	.034

TABLE XIV

FARMERS - 96 PEN SATURATES

Group Freq.		Δ% T	X %T/CH_2 (%T @ 2853
First Order			
(5H)	700	5	.088
$(CH_2)n = 4$	720	24	.421
4 or 5(H)	750	15	.263
4 or 5(H)	760	11	.193
3(H) ADJ	785	8	.140
2(H) ADJ	810	12	.210
1(H) ADJ	870	10	.175
(S=O) R-S-R	1020	9	.158
CH (AROM)	1030	11	.193
(SO_3H) S-R	1060	8	.140
Second Order			
SO_2 Ester	1165	21	.368
Ester (SO_2)	1260	23	.404
CO, OH or SO_2	1300-1320	30	.526
$C-(CH_3)n$	1368	47	.825
$C=CH_2$	1380	66	1.158
CH_2	1460	82	1.439
C=C (AROM)	1600	21	.368
C=C (olefin) -	1660	12	.210
C=O	1700	12	.210
C=O	1760	3	.053
Third Order			
CH	2720	3	.053
CH_2	2853	57	1.000
CH_3	2872	42	.737
CH_2	2926	76	1.333
CH_3	2962	54	.947
Fourth Order			
CH_2	2853	55	.965
CH_3	2872	42	.737
CH_2	2926	74	1.298
CH_3	2962	52	.912
=C-H	3030	4	.070
OH	3300	1	.018

TABLE XV

(Whole Asphalt 6-30-64)
Composite of Farmers
100-120 Pen

Group Freq.		Δ% T	X %T/CH_2 (%T @ 2853
<u>First Order</u>			
(5H)	700	3	.048
$(CH_2)n = 4$	720	23	.371
4 or 5(H)	750	23	.371
4 or 5(H)	760	21	.339
3(H) ADJ	785	15	.242
2(H) ADJ	810	25	.403
1(H) ADJ	870	22	.355
(S=O) R-S-R	1020	7	.113
CH (AROM)	1030	10	.161
(SO_3H) S-R	1060	8	.129
<u>Second Order</u>			
SO_2 Ester	1165	27	.435
Ester (SO_2)	1260	32	.516
CO, OH or SO_2	1300-1320	43	.694
$C-(CH_3)n$	1368	58	.935
$C-CH_3$	1380	73	1.177
CH_2	1460	85	1.371
C=C (AROM)	1600	39	.628
C=C (olefin) -	1660	20	.323
C=O	1700	10	.162
C=O	1760	5	.081
<u>Third Order</u>			
CH	2720	5	.081
CH_2	2853	62	1.000
CH_3	2872	53	.855
CH_2	2926	74	1.194
CH_3	2962	61	.984
<u>Fourth Order</u>			
CH_2	2853	59	.952
CH_3	2872	51	.823
CH_2	2926	72	1.177
CH_3	2962	61	.984
=C-H	3030	8	.129
OH	3300	3	.048

TABLE XVI

(Asphaltics 6-30-64)
Composite of Farmers
100-120 Pen 27%

Group Freq.		Δ % T	X %T/CH_2 (%T @ 2853
<u>First Order</u>			
(5H)	700	3	.061
$(CH_2)n = 4$	720	5	.102
4 or 5(H)	750	6	.122
4 or 5(H)	760	7	.143
3(H) ADJ	785	7	.143
2(H) ADJ	810	6	.122
1(H) ADJ	870	7	.143
(S=O) R-S-R	1020	6	.122
CH (AROM)	1030	7	.143
(SO_3H) S-R	1060	6	.122
<u>Second Order</u>			
SO_2 Ester	1165	5	.102
Ester (SO_2)	1260	8	.163
CO, OH or SO_2	1300-1320	11	.224
$C-(CH_3)n$	1368	16	.327
$C-CH_3$	1380	22	.449
CH_2	1460	31	.633
C=C (AROM)	1600	13	.265
C=C (olefin) -	1660	6	.122
C=O	1700	6	.122
C=O	1760	2	.041
<u>Third Order</u>			
CH	2720	4	.082
CH_2	2853	49	1.000
CH_3	2872	40	.817
CH_2	2926	63	1.286
CH_3	2962	49	1.000
<u>Fourth Order</u>			
CH_2	2853	44	.898
CH_3	2872	35	.714
CH_2	2926	57	1.163
CH_3	2962	44	.898
=C-H	3030	5	.102
OH	3300	2	.041

TABLE XVII

(Cyclics June 30-64)
Composite of Farmers
100-120 Pen 23%

Group Freq.		$\triangle$ % T	X %T/CH_2 (%T @ 2853
<u>First Order</u>			
(5H)	700	5	.094
$(CH_2)n = 4$	720	18	.339
4 or 5(H)	750	27	.509
4 or 5(H)	760	25	.472
3(H) ADJ	785	18	.339
2(H) ADJ	810	29	.547
1(H) ADJ	870	21	.396
(S=O) R-S-R	1020	22	.415
CH (AROM)	1030	23	.434
(SO_3H) S-R	1060	13	.245
<u>Second Order</u>			
SO_2 Ester	1165	34	.642
Ester (SO_2)	1260	38	.717
CO, OH or SO_2	1300-1320	47	.887
$C-(CH_3)n$	1368	58	1.094
$C-CH_3$	1380	70	1.321
CH_2	1460	82	1.547
C=C (AROM)	1600	47	.887
C=C (olefin) -	1660	28	.528
C=O	1700	31	.585
C=O	1760	22	.415
<u>Third Order</u>			
CH	2720	5	.094
CH_2	2853	53	1.000
CH_3	2872	50	.943
CH_2	2926	71	1.340
CH_3	2962	61	1.151
<u>Fourth Order</u>			
CH_2	2853	51	.961
CH_3	2872	48	.906
CH_2	2926	70	1.321
CH_3	2962	60	1.132
=C-H	3030	10	.189
OH	3300	6	.113

TABLE XVIII

(Saturates 6-30-64)
Composite of Farmers
100-120 Pen 51%

Group Freq.		% T	X %T.CH_2 (%T @ 2853
<u>First Order</u>			
(5H)	700	7	.113
$(CH_2)n = 4$	720	26	.419
4 or 5(H)	750	18	.290
4 or 5(H)	760	15	.242
3(H) ADJ	785	10	.161
2(H) ADJ	810	16	.258
1(H) ADJ	870	14	.226
(S=O) R-S-R	1020	14	.226
CH (AROM)	1030	16	.258
(SO_3H) S-R	1060	10	.161
<u>Second Order</u>			
SO_2 Ester	1165	33	.532
Ester (SO_2)	1260	35	.565
CO, OH or SO_2	1300-1320	43	.694
$C-(CH_3)n$	1368	60	.968
$C-CH_3$	1380	73	1.177
CH_2	1460	81	1.306
C=C (AROM)	1600	37	.597
C=C (olefin) -	1660	21	.339
C=O	1700	24	.387
C=O	1760	7	.113
<u>Third Order</u>			
CH	2720	4	.065
CH_2	2853	62	1.000
CH_3	2872	48	.774
CH_2	2926	80	1.290
CH_3	2962	60	.968
<u>Fourth Order</u>			
CH_2	2853	61	.984
CH_3	3872	49	.790
CH_2	2926	78	1.258
CH_3	2962	59	.952
=C-H	3030	5	.081
OH	3300	2	.032

TABLE XIX

(Whole Asphalt)
Phillips 100-120

Group Freq.		Δ % T	X %T/CH_2 (%T @ 2853
<u>First Order</u>			
(5H)	700	5	.083
$(CH_2)n = 4$	720	26	.433
4 or 5(H)	750	26	.433
4 or 5(H)	760	22	.367
3(H) ADJ	785	16	.267
2(H) ADJ	810	26	.433
1(H) ADJ	870	22	.367
(S=O) R-S-R	1020	13	.217
CH (AROM)	1030	16	.267
(SO_3H) S-R	1060	12	.200
<u>Second Order</u>			
SO_2 Ester	1165	31	.517
Ester (SO_2)	1260	37	.617
CO, OH or SO_2	1300-1320	46	.767
$C-(CH_3)n$	1368	61	1.017
$C-CH_3$	1380	75	1.250
CH_2	1460	85	1.417
C=C (AROM)	1600	41	.683
C=C (olefin) -	1660	23	.383
C=O	1700	12	.200
C=O	1760	6	.100
<u>Third Order</u>			
CH	2720	4	.083
CH_2	2853	60	1.000
CH_3	2872	52	.867
CH_2	2926	76	1.267
CH_3	2962	58	.967
<u>Fourth Order</u>			
CH_2	2853	57	.950
CH_3	2872	47	.783
CH_2	2926	75	1.250
CH_3	2962	56	.933
=C-H	3030	7	.117
OH	3300	2	.033

TABLE XX

Cyclics 20%
Phillips 100-120 Pen

Group Freq.		Δ % T	X %T/CH_2 (%T @ 2853
<u>First Order</u>			
(5H)	700	6	.105
$(CH_2)n$ = 4	720	19	.333
4 or 5(H)	750	30	.526
4 or 5(H)	760	27	.474
3(H) ADJ	785	19	.333
2(H) ADJ	810	30	.526
1(H) ADJ	870	21	.368
(S=O) R-S-R	1020	18	.316
CH (AROM)	1030	21	.368
(SO_3H) S-R	1060	13	.228
<u>Second Order</u>			
SO_2 Ester	1165	33	.579
Ester (SO_2)	1260	36	.632
CO, OH or SO_2	1300-1320	44	.772
C-$(CH_3)n$	1368	56	.982
C-CH_3	1380	59	1.211
CH_2	1460	79	1.386
C=C (AROM)	1600	43	.754
C=C (olefin) -	1660	25	.438
C=O	1700	25	.438
C=O	1760	10	.175
<u>Third Order</u>			
CH	2720	6	.105
CH_2	2853	57	1.000
CH_3	2872	54	.947
CH_2	2926	72	1.263
CH_3	2962	64	1.123
<u>Fourth Order</u>			
CH_2	2853	56	.982
CH_3	2872	51	.895
CH_2	2926	70	1.228
CH_3	2962	62	1.088
=C-H	3030	11	.193
OH	3300	5	.088

TABLE XXI

(Asphaltics 35%)
Phillips 100-120 Pen

Group Freq.		Δ % T	X %T/CH_2 (%T @ 2853
<u>First Order</u>			
(5H)	700	5	.068
$(CH_2)n = 4$	720	11	.151
4 or 5(H)	750	12	.164
4 or 5(H)	760	11	.151
3(H) ADJ	785	9	.123
2(H) ADJ	810	12	.164
1(H) ADJ	870	11	.151
(S=O R-S-R	1020	8	.110
CH (AROM)	1030	9	.123
(SO_3H) S-R	1060	7	.096
<u>Second Order</u>			
SO_2 Ester	1165	17	.233
Ester (SO_2)	1260	21	.288
CO, OH or SO_2	1300-1320	26	.356
C-$(CH_3)n$	1368	32	.438
C-CH_3	1380	41	.562
CH_2	1460	59	.808
C=C (AROM)	1600	26	.356
C=C (olefin) -	1660	14	.192
C=O	1700	11	.151
C=O	1760	3	.041
	1900	2	.027
<u>Third Order</u>			
CH	2720	9	.123
CH_2	2853	73	1.000
CH_3	2872	65	.890
CH_2	2926	83	1.137
CH_3	2962	64	.877
<u>Fourth Order</u>			
CH_2	2853	69	.945
CH_3	2872	62	.849
CH_2	2926	80	1.096
CH_3	2962	69	.945
=C-H	3030	15	.205
OH	3300	5	.068

TABLE XXII

Saturates 45%
Phillips 100-120 Pen

Group Freq.		$\triangle$ % T	X %T/CH_2 (%T @ 2853
First Order			
(5H)	700	3	.044
$(CH_2)n = 4$	720	29	.426
4 or 5 (H)	750	19	.279
4 or 5 (H)	760	15	.221
3(H) ADJ	785	10	.147
2(H) ADJ	810	16	.235
1(H) ADJ	870	12	.176
(S=O) R-S-R	1020	11	.162
CH (AROM)	1030	14	.206
(SO_3H) S-R	1060	9	.132
Second Order			
SO_2 Ester	1165	24	.353
Ester (SO_2)	1260	28	.412
CO, OH or SO_2	1300-1320	42	.618
$C-(CH_3)n$	1368	61	.897
$C-CH_3$	1380	78	1.147
CH_2	1460	99	1.456
C=C (AROM)	1600	27	.397
C=C (olefin) -	1660	14	.206
C=O	1700	15	.221
C=O	1760	5	.074
Third Order			
CH	2720	5	.074
CH_2	2853	68	1.000
CH_3	2872	55	.809
CH_2	2926	85	1.250
CH_3	2962	65	.956
Fourth Order			
CH_2	2853	66	.971
CH_3	2872	53	.779
CH_2	2926	82	1.206
CH_3	2962	63	.926
=C-H	3030	5	.074
OH	3300	2	.029

TABLE XXIII

Humble Whole Asphalt 100-120 Pen

Group Freq.		$\triangle$ % T	X %T/CH_2 (%T @ 2853
<u>First Order</u>			
(5H)	700	3	.054
$(CH_2)n = 4$	720	21	.382
4 or 5 (H)	750	22	.400
4 or 5 (H)	760	20	.364
3(H) ADJ	785	14	.254
2(H) ADJ	810	24	.436
1(H) ADJ	870	21	.382
(S=O) R-S-R	1020	12	.218
CH (AROM)	1030	13	.236
(SO_3H) S-R	1060	9	.164
<u>Second Order</u>			
SO_2 Ester	1165	26	.473
Ester (SO_2)	1260	31	.564
CO, OH, or SO_2	1300-1320	42	.764
C-$(CH_3)n$	1368	58	1.054
C-CH_3	1380	72	1.309
CH_2	1460	84	1.527
C=C (AROM)	1600	37	.673
C=C (olefin) -	1660	18	.327
C=O	1700	9	.164
C=O	1760	5	.091
<u>Third Order</u>			
CH	2720	5	.091
CH_2	2853	55	1.000
CH_3	2872	44	.800
CH_2	2926	72	1.309
CH_3	2962	56	1.018
<u>Fourth Order</u>			
CH_2	2853	53	.964
CH_3	2872	43	.782
CH_2	2926	69	1.254
CH_3	2962	52	.945
=C-H	3030	5	.091
OH	3300	2	.036

TABLE XXIV

Asphaltics
34% Comp. of Humble
100-120 Pen

Group Freq.		△ % T	X %T/CH_2 (%T @ 2853
First Order			
(5H)	700	3	.053
$(CH_2)n = 4$	720	14	.246
4 or 5 (H)	750	17	.298
4 or 5 (H)	760	15	.263
3(H) ADJ	785	11	.193
2(H) ADJ	810	19	.333
1(H) ADJ	870	18	.316
(S=O) R-S-R	1020	11	.193
CH (AROM)	1030	14	.246
(SO_3H) S-R	1060	8	.140
Second Order			
SO_2 Ester	1165	26	.456
Ester (SO_2)	1260	31	.544
CO, OH, or SO_2	1300-1320	39	.684
C-$(CH_3)n$	1368	46	.807
C-CH_3	1380	56	.982
CH_2	1460	66	1.158
C=C (AROM)	1600	39	.684
C=C (olefin) -	1660	20	.351
C=O	1700	18	.316
C=O	1760	6	.105
Third Order			
CH	2720	8	.140
CH_2	2853	57	1.000
CH_3	2872	50	.877
CH_2	2926	69	1.210
CH_3	2962	57	1.000
Fourth Order			
CH_2	2853	53	.930
CH_3	2872	48	.842
CH_2	2926	68	1.193
CH_3	2962	54	.947
=C-H	3030	15	.263
OH	3300	5	.088

TABLE XXV

Humble Cyclics
19% Comp. 100-120 Pen

Group Freq.		Δ % T	X %T/CH_2 (%T @ 2853
<u>First Order</u>			
(5H)	700	6	.107
$(CH_2)n = 4$	720	12	.214
4 or 5 (H)	750	22	.393
4 or 5 (H)	760	19	.339
3(H) ADJ	785	14	.250
2(H) ADJ	810	23	.411
1(H) ADJ	870	17	.304
(S=O) R-S-R	1020	17	.304
CH (AROM)	1030	19	.339
(SO_3H) S-R	1060	10	.178
<u>Second Order</u>			
SO_2 Ester	1165	25	.446
Ester (SO_2)	1260	28	.500
CO, OH, or SO_2	1300-1320	36	.643
$C-(CH_3)n$	1368	44	.786
$C-CH_3$	1380	59	1.054
CH_2	1460	72	1.286
C=C (AROM)	1600	35	.625
C=C (olefin) -	1660	22	.393
C=O	1700	22	.393
C=O	1760	8	.143
<u>Third Order</u>			
CH	2720	5	.089
CH_2	2853	56	1.000
CH_3	2872	54	.964
CH_2	2926	77	1.375
CH_3	2962	67	1.196
<u>Fourth Order</u>			
CH_2	2853	57	1.018
CH_3	2872	53	.946
CH_2	2926	77	1.375
CH_3	2962	67	1.196
=C-H	3030	13	.232
OH	3300	7	.125

TABLE XXVI

Humble Saturates
47% 100-120 Pen

Group Freq.		$\triangle$ % T	X %T/CH_2 (%T @ 2853
First Order			
(5H)	700	5	.077
$(CH_2)n = 4$	720	24	.369
4 or 5 (H)	750	16	.246
4 or 5 (H)	760	12	.185
3(H) ADJ	785	8	.123
2(H) ADJ	810	14	.215
1(H) ADJ	870	11	.169
(S=O) R-S-R	1020	11	.169
CH (AROM)	1030	13	.200
(SO_3H) S-R	1060	8	.123
Second Order			
SO_2 Ester	1165	22	.338
Ester (SO_2)	1260	26	.400
CO, OH, or SO_2	1300-1320	34	.523
$C-(CH_3)n$	1368	53	.815
$C-CH_3$	1380	71	1.092
CH_2	1460	82	1.262
C=C (AROM)	1600	26	.400
C=C (olefin) -	1660	15	.231
C=O	1700	17	.262
C=O	1760	5	.077
Third Order			
CH	2720	4	.062
CH_2	2853	65	1.000
CH_3	2872	54	.831
CH_2	2926	81	1.246
CH_3	2962	64	.985
Fourth Order			
CH_2	2853	64	.985
CH_3	2872	54	.831
CH_2	2926	82	1.262
CH_3	2962	63	.969
=C-H	3030	4	.062
OH	3300	2	.031

TABLE XXVII

Diamond 100-120 Pen
Whole Asphalt

Group Freq.		△ % T	X %T/CH_2 %T @ 2853
First Order			
(5H)	700	4	.066
$(CH_2)n$ = 4	720	25	.410
4 or 5(H)	750	25	.410
4 or 5(H)	760	23	.377
3(H) ADJ	785	16	.262
2(H) ADJ	810	24	.393
1(H) ADJ	870	19	.311
(S=O) R-S-R	1020	12	.197
CH (AROM)	1030	14	.230
(SO_3H) S-R	1060	10	.164
Second Order			
SO_2 Ester	1165	33	.541
Ester (SO_2)	1260	39	.639
CO, OH or SO_2	1300-1320	49	.803
C-$(CH_3)n$	1368	61	1.000
C-CH_3	1380	74	1.213
CH_2	1460	84	1.377
C=C (AROM)	1600	45	.738
C=C (olefin) -	1660	30	.492
C=O	1700	14	.230
C=O	1760	7	.115
Third Order			
CH	2720	5	.082
CH_2	2853	61	1.000
CH_3	2872	49	.803
CH_2	2926	79	1.295
CH_3	2962	60	.984
Fourth Order			
CH_2	2853	58	.951
CH_3	2872	47	.770
CH_2	2926	77	1.262
CH_3	2962	58	.951
=C-H	3030	7	.115
OH	3300	3	.049

TABLE XXVIII

Asphaltics
34% Diamond Comp.
100-120 Pen

Group Freq.		Δ % T	X %T/CH_2 (%T @2853
First Order			
(5H)	700	5	.082
$(CH_2)n$ = 4	720	7	.115
4 or 5 (H)	750	8	.131
4 or 5 (H)	760	6	.098
3(H) ADJ	785	5	.082
2(H) ADJ	810	7	.115
1(H) ADJ	870	6	.098
(S=O) R-S-R	1020	6	.098
CH (AROM)	1030	7	.115
(SO_3H) S-R	1060	5	.082
Second Order			
SO_2 Ester	1165	8	.131
Ester (SO_2)	1260	11	.180
CO, OH or SO_2	1300-1320	14	.230
C-$(CH_3)n$	1368	17	.279
C-CH_3	1380	23	.377
CH_2	1460	35	.574
C=C (AROM)	1600	15	.246
C=C (olefin) -	1660	10	.164
C=O	1700	6	.098
C=O	1760	2	.033
Third Order			
CH	2720	6	.098
CH_2	2853	61	1.000
CH_3	2872	46	.754
CH_2	2926	74	1.213
CH_3	2962	56	.918
Fourth Order			
CH_2	2853	51	.836
CH_3	2872	40	.656
CH_2	2926	67	1.098
CH_3	2962	50	.820
=C-H	3030	5	.082
OH	3300	3	.049

TABLE XXIX

Cyclics
Diamond 100-120 Pen
26%

Group Freq.		△ % T	X %T/CH_2 (%T @ 2853
First Order			
(5H)	700	5	.085
$(CH_2)n = 4$	720	19	.322
4 or 5 (H)	750	28	.475
4 or 5 (H)	760	23	.390
3(H) ADJ	785	16	.271
2(H) ADJ	810	26	.441
1(H) ADJ	870	16	.271
(S=O) R-S-R	1020	19	.322
CH (AROM)	1030	21	.356
(SO_3H) S-R	1060	10	.169
Second Order			
SO_2 Ester	1165	31	.525
Ester (SO_2)	1260	34	.576
CO, OH or SO_2	1300-1320	41	.695
C-$(CH_3)n$	1368	54	.915
C-CH_3	1380	70	1.186
CH_2	1460	84	1.424
C=C (AROM)	1600	36	.610
C=C (olefin) -	1660	24	.407
C=O	1700	23	.390
C=O	1760	10	.169
Third Order			
CH	2720	5	.085
CH_2	2853	59	1.000
CH_3	2872	55	.932
CH_2	2926	79	1.339
CH_3	2962	68	1.153
Fourth Order			
CH_2	2853	59	1.000
CH_3	2872	54	.915
CH_2	2926	79	1.339
CH_3	2962	68	1.153
=C-H	3030	9	.153
OH	3300	5	.085

TABLE XXX

40% Saturates
Diamond Comp.
100-120 Pen

Group Freq.		Δ % T	X %T/CH_2 (%T @ 2853
First Order			
(5H)	700	3	.053
$(CH_2)n$ = 4	720	31	.544
4 or 5 (H)	750	19	.333
4 or 5 (H)	760	15	.263
3(H) ADJ	785	11	.193
2(H) ADJ	810	15	.263
1(H) ADJ	870	10	.175
(S=O) R-S-R	1020	14	.246
CH (AROM)	1030	15	.263
(SO_3H) S-R	1060	10	.175
Second Order			
SO_2 Ester	1165	29	.509
Ester (SO_2)	1260	33	.579
CO, OH, or SO_2	1300-1320	41	.719
$C-(CH_3)n$	1368	58	1.018
$C-CH_3$	1380	74	1.298
CH_2	1460	89	1.561
C=C (AROM)	1600	29	.509
C=C (olefin) -	1660	22	.386
C=O	1700	17	.298
C=O	1760	5	.088
Third Order			
CH	2720	4	.070
CH_2	2853	57	1.000
CH_3	2872	44	.772
CH_2	2926	77	1.351
CH_3	2962	53	.930
Fourth Order			
CH_2	2853	55	.965
CH_3	2872	41	.719
CH_2	2926	75	1.316
CH_3	2962	51	.895
=C-H	3030	3	.053
OH	3300	2	.035

TABLE XXXI

Big West
110 Pen
Whole Asphalt
#71564

Group Freq.		Δ% T	X %T/CH_2 (%T @ 2853
First Order			
(5H)	700	9	.164
$(CH_2)n = 4$	720	28	.509
4 or 5 (H)	750	40	.727
4 or 5 (H)	760	37	.673
3(H) ADJ	785	30	.545
2(H) ADJ	810	43	.782
1(H) ADJ	870	37	.673
(S=O) R-S-R	1020	14	.255
CH (AROM)	1030	21	.382
(SO_3H) S-R	1060	13	.236
Not identifiable	950	6	.109
Second Order			
SO_2 Ester	1165	32	.582
Ester (SO_2)	1260	35	.636
CO, OH or SO_2	1300-1320	47	.855
$C-(CH_3)n$	1368	57	1.036
$C-CH_3$	1380	72	1.309
CH_2	1460	83	1.509
C=C (AROM)	1600	52	.945
C=C (olefin) -	1660	18	.327
C=O	1700	14	.255
C=O	1760	11	.200
Third Order			
CH	2720	5	.091
CH_2	2853	55	1.000
CH_3	2872	48	.873
CH_2	2926	65	1.182
CH_3	2962	56	1.018
Fourth Order			
CH_2	2853	55	1.000
CH_3	2872	48	.873
CH_2	2926	65	1.182
CH_3	2962	55	1.000
=C-H	3030	14	.255
OH	3300	3	.055

TABLE XXXII

Big West
26% Asphaltics
#2064

Group Freq.		Δ % T	X %T/CH_2 (%T @ 2853
<u>First Order</u>			
(5H)	700	6	.182
$(CH_2)n = 4$	720	5	.152
4 or 5 (H)	750	8	.242
4 or 5 (H)	760	9	.273
3(H) ADJ	785	9	.273
2(H) ADJ	810	9	.273
1(H) ADJ	870	9	.273
(S=O) R-S-R	1020	6	.182
CH (AROM)	1030	7	.212
(SO_3H) S-R	1060	5	.152
Not identifiable	950	3	.091
<u>Second Order</u>			
SO_2 Ester	1165	9	.273
Ester (SO_2)	1260	9	.273
CO, OH or SO_2	1300-1320	11	.333
C-(CH_3)n	1368	13	.394
C-CH_3	1380	18	.545
CH_2	1460	26	.788
C=C (AROM)	1600	13	.394
C=C (olefin) -	1660	6	.182
C=O	1700	5	.152
C=O	1760	3	.091
<u>Third Order</u>			
CH	2720	3	.091
CH_2	2853	33	1.000
CH_3	2872	29	.879
CH_2	2926	53	1.606
CH_3	2962	36	1.091
<u>Fourth Order</u>			
CH_2	2853	32	.970
CH_3	2872	28	.848
CH_2	2926	51	1.546
CH_3	2962	35	1.061
=C-H	3030	8	.242
OH	3300	2	.061

TABLE XXXIII

Big West
Cyclics
110 Pen Sample
from Stream by
Westvelt 46%

Group Freq.		Δ% T	X %T/CH_2 (%T @ 2853
First Order			
(5H)	700	10	.192
$(CH_2)n$ = 4	720	12	.231
4 or 5(H)	750	42	.808
4 or 5(H)	760	39	.750
3(H) ADJ	785	29	.558
2(H) ADJ	810	43	.827
1(H) ADJ	870	35	.673
(S=O) R-S-R	1020	17	.327
CH (AROM)	1030	23	.442
(SO_3H) S-R	1060	14	.269
Second Order			
SO_2 Ester	1165	44	.846
Ester (SO_2)	1260	40	.769
CO, OH or SO_2	1300-1320	49	.942
C-$(CH_3)n$	1368	62	1.192
C-CH_3	1380	23	1.404
CH_2	1460	84	1.615
C=C (AROM)	1600	57	1.096
C=C (olefin) -	1660	28	.538
C=O	1700	44	.846
C=O	1760	15	.288
Third Order			
CH	2720	5	.096
CH_2	2853	52	1.000
CH_3	2872	50	.962
CH_2	2926	72	1.385
CH_3	2962	62	1.192
Fourth Order			
CH_2	2853	53	1.019
CH_3	2872	50	.962
CH_2	2926	73	1.404
CH_3	2962	62	1.192
=C-H	3030	16	.308
OH	3300	5	.096

TABLE XXXIV

Big West
Saturates 28%
110 Pen
Stream by Westwell

Group Freq.		Δ % T	X %T/CH_2 (%T @ 2853
<u>First Order</u>			
(5H)	700	7	.123
$(CH_2)n = 4$	720	35	.614
4 or 5 (H)	750	24	.421
4 or 5 (H)	760	21	.368
3(H) ADJ	785	16	.281
2(H) ADJ	810	24	.421
1(H) ADJ	870	20	.351
(S=O) R-S-R	1020	13	.228
CH (AROM)	1030	16	.281
(SO_3H) S-R	1060	13	.228
<u>Second Order</u>			
SO_2 Ester	1165	25	.439
Ester (SO_2)	1260	29	.509
CO, OH or SO_2	1300-1320	37	.649
C-(CH_3)n	1368	52	.912
C-CH_3	1380	69	1.211
CH_2	1460	83	1.456
C=C (AROM)	1600	34	.596
C=C (olefin) -	1660	18	.316
C=O	1700	20	.351
C=O	1760	7	.123
<u>Third Order</u>			
CH	2720	4	.071
CH_2	2853	58	1.000
CH_3	2872	40	.702
CH_2	2926	75	1.316
CH_3	2962	49	.860
<u>Fourth Order</u>			
CH_2	2853	56	.982
CH_3	2872	38	.667
CH_2	2926	74	1.298
CH_3	2962	47	.825
=C-H	3030	5	.088
OH	3300	2	.035

TABLE XXXV

Whole Asphalt
Conoco 100-120 Pen

Group Freq.		△ % T	X %T/CH_2 (%T @ 2853
<u>First Order</u>			
(5H)	700	5	.106
$(CH_2)n$ = 4	720	23	.489
4 or 5(H)	750	33	.702
4 or 5(H)	760	31	.660
3(H) ADJ	785	23	.489
2(H) ADJ	810	37	.787
1(H) ADJ	870	32	.681
(S=O) R-S-R	1020	18	.383
CH (AROM)	1030	23	.489
(SO_3H) S-R	1060	15	.319
<u>Second Order</u>			
SO_2 Ester	1165	30	.638
Ester (SO_2)	1260	35	.745
CO, OH or SO	1300-1320	46	.979
$C-(CH_3)n$	1368	58	1.234
$C-CH_3$	1380	70	1.489
CH_2	1460	79	1.681
C=C (AROM)	1600	49	1.043
C=C (olefin)	1660	28	.596
C=O	1700	14	.298
C=O	1760	8	.170
<u>Third Order</u>			
CH	2720	6	.128
CH_2	2853	47	1.000
CH_3	2872	40	.851
CH_2	2926	60	1.277
CH_3	2962	49	1.043
<u>Fourth Order</u>			
CH_2	2853	43	.915
CH_3	2872	36	.766
CH_2	2926	57	1.213
CH_3	2962	45	.957
=C-H	3030	7	.149
OH	3300	3	.064

TABLE XXXVI

Asphaltics
38% Conoco Composite
100-120 Pen

Group Freq.		Δ % T	X %T/CH_2 (%T @ 2853
<u>First Order</u>			
(5H)	700	4	.070
$(CH_2)n = 4$	720	8	.140
4 or 5 (H)	750	11	.193
4 or 5 (H)	760	11	.193
3(H) ADJ	785	7	.123
2(H) ADJ	810	12	.211
1(H) ADJ	870	12	.211
(S=O) R-S-R	1020	6	.105
CH (AROM)	1030	8	.140
(SO_3H) S-R	1060	6	.105
<u>Second Order</u>			
SO_2 Ester	1165	12	.211
Ester (SO_2)	1260	15	.263
CO, OH or SO_2	1300-1320	20	.351
$C-(CH_3)n$	1368	25	.439
$C-CH_3$	1380	33	.579
CH_2	1460	42	.737
C=C (AROM)	1600	22	.386
C=C (olefin)	1660	10	.175
C=O	1700	7	.123
C=O	1760	3	.052
<u>Third Order</u>			
CH	2720	7	.123
CH_2	2853	57	1.000
CH_3	2872	52	.912
CH_2	2926	71	1.246
CH_3	2962	60	1.053
<u>Fourth Order</u>			
CH_2	2853	52	.912
CH_3	2872	46	.807
CH_2	2926	67	1.175
CH_3	2962	55	.965
=C-H	3030	11	.193
OH	3300	2	.035

TABLE XXXVII

Cyclics
Conoco 100-120 Pen
39%

Group Freq.		% T	X %T/CH_2 (%T @ 2853
First Order			
(5H)	700	7	.135
$(CH_2)n = 4$	720	22	.423
4 or 5 (H)	750	44	.846
4 or 5 (H)	760	41	.788
3(H) ADJ	785	30	.577
2(H) ADJ	810	47	.904
1(H) ADJ	870	36	.692
(S=O) R-S-R	1020	22	.423
CH (AROM)	1030	27	.519
(SO_3H) S-R	1060	16	.308
Second Order			
SO_2 Ester	1165	33	.635
Ester (SO_2)	1260	36	.692
CO, OH or SO_2	1300-1320	45	.865
$C-(CH_3)n$	1368	56	1.077
$C-CH_3$	1380	73	1.404
CH_2	1460	83	1.596
C=C (AROM)	1600	52	1.000
C=C (olefin)	1660	30	.577
C=O	1700	24	.462
C=O	1760	12	.231
Third Order			
CH	2720	6	.115
CH_2	2853	52	1.000
CH_3	2872	50	.962
CH_2	2926	73	1.404
CH_3	2962	63	1.212
Fourth Order			
CH_2	2853	49	.942
CH_3	2872	48	.923
CH_2	2926	71	1.365
CH_3	2962	61	1.173
=C-H	3030	16	.308
OH	3300	3	.058

TABLE XXXVIII

Saturates
Conoco 100-120 Pen
23%

Group Freq.		Δ % T	X %T/CH_2 (%T @ 2853
<u>First Order</u>			
(5H)	700	3	.052
$(CH_2)n = 4$	720	32	.561
4 or 5 (H)	750	20	.351
4 or 5 (H)	760	19	.333
3(H) ADJ	785	18	.316
2(H) ADJ	810	18	.316
1(H) ADJ	870	15	.263
(S=O) R-S-R	1020	13	.228
CH (AROM)	1030	15	.263
(SO_3) S-R	1060	11	.193
<u>Second Order</u>			
SO_2 Ester	1165	25	.439
Ester (SO_2)	1260	29	.509
CO, OH or SO_2	1300-1320	37	.649
$C-(CH_3)n$	1368	56	.982
$C-CH_3$	1380	72	1.263
CH_2	1460	86	1.509
C=C (AROM)	1600	31	.544
C=C (olefin)	1660	22	.386
C=O	1700	17	.298
C=O	1760	5	.088
<u>Third Order</u>			
CH	2720	5	.088
CH_2	2853	57	1.000
CH_3	2872	44	.772
CH_2	2926	76	1.333
CH_3	2962	53	.930
<u>Fourth Order</u>			
CH_2	2853	53	.930
CH_3	2872	39	.684
CH_2	2926	72	1.263
CH_3	2962	50	.877
=C-H	3030	5	.088
OH	3300	3	.053

PART I-D

DEVELOPMENT OF QUANTITATIVE PROCEDURES FOR ADHESIVE AGENTS IN BITUMINOUS MATERIALS

Introduction

Should the use of adhesive agents become general, quality control tests will have to be performed for these agents. At the present time there is no suitable quantitative procedure capable of giving the adhesive agent concentration in asphalt. The aim of this study was to determine the feasibility of quantitative infra-red analysis.

Although the function of adhesive agents is not clearly understood, all currently approved agents contain relatively high concentrations of primary and secondary amines, and there is evidence also of considerable amounts of ammonia in several. The amine groups have absorption bands in the 3600-3900 wave number region and although the intensity of these bands varies from one amine to another, the strongest band in all cases is of sufficient intensity to permit quantitative study. This is fortunate since asphalt and its solvents, benzene, carbon tetrachloride and carbon disulfide are optically transparent in this same region. Carbon tetrachloride has proven to be the most versatile solvent; however, it undergoes an additional reaction with certain aromatic amines such as aniline. The reaction rate seems to be so slow that an analysis can still be carried out before any appreciable amount of the amine has reacted. This will be discussed in more detail later. Benzene has a strong absorption band between 3000 and 3300 wave numbers which may minimize the intensity of the NH stretch region. Carbon disulfide was not studied to any degree because of its very disagreeable nature.

The best procedure found was to compare the absorption of the unknown with that of a suitable standard, keeping the optical path length the same. The standard amine must be similar in character to the unknown since vi-

brational frequencies and intensities are affected by adjacent groups. In certain cases, samples of adhesive agent could serve as standards for comparison with the asphalts. In other cases a preliminary analysis must thus be made to determine whether the amine is aliphatic or aromatic and also whether it is primary, secondary or tertiary. It is of special importance that the sample and standard are free of water since a slight trace will give rise to an OH stretching frequency which intensifies the NH and NH_2 region and gives incorrect results.

Experimental

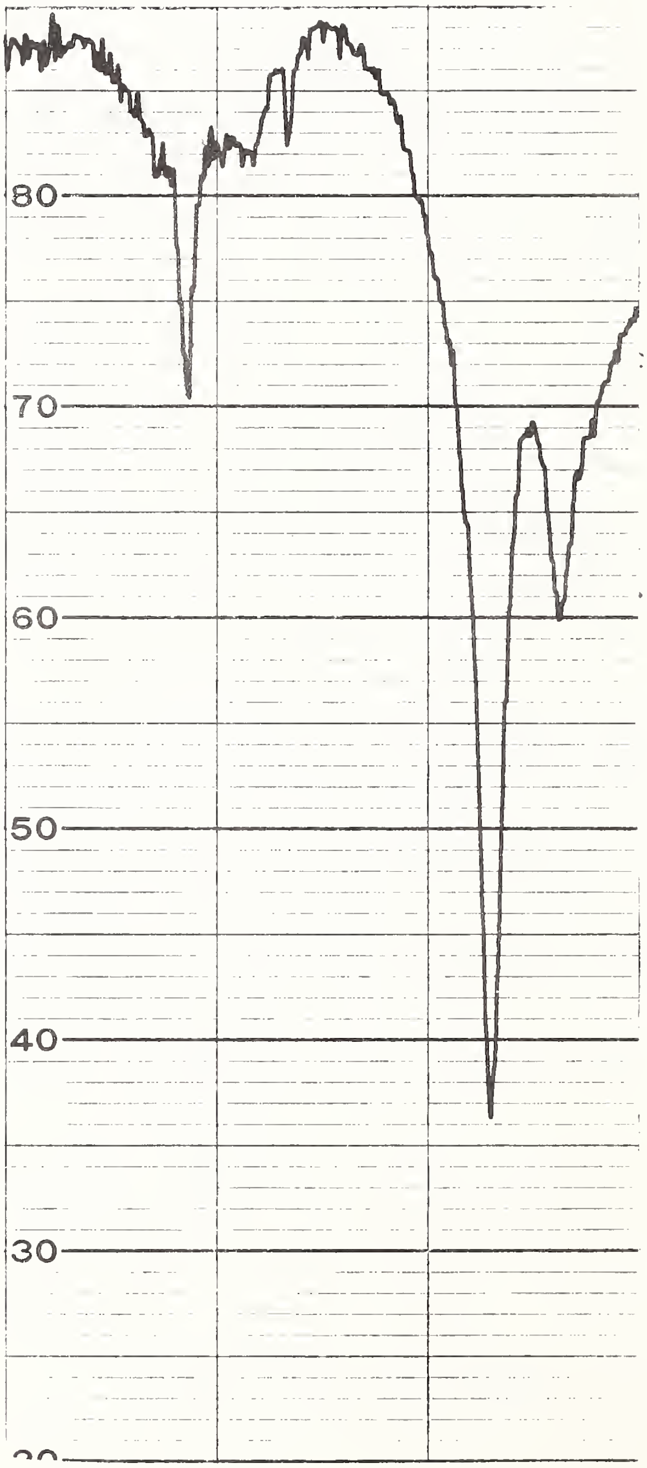
Solutions of aniline and carbon tetrachloride from 1.0:1.0 ratio by volume to a 1.0: 0.005 ratio were prepared. Infrared spectra from the fourth order ie: 3000-4000 wave numbers were run. The absorption of the solutions was plotted against concentration and yielded a straight line in accordance with Beer's Law.

A 3mm Beckman variable path cell was used for unknowns of hexylamine, aniline and an adhesive agent (Arosurf AA-11), which were prepared by co-workers. The two samples of hexylamine were reported at .56% and 2.02%. The known values were .50% and 2.00%. The evaluation of this compound is thus considered satisfactory. The sample to be analyzed was dissolved in carbon tetrachloride and the concentration and cell thickness were adjusted to give approximately 50% for the transmittance. Standards were then diluted to give a reading between 80% and 20% so that the unknown was between two or more measurements on the standards. Plate 1 shows the pertinent part of the spectra for hexylamine while Plate 2 shows the control graph.

In the case of aniline, the determination of the unknowns in all cases gave concentrations in excess of the correct amount. The only procedural difference was the time between solution preparation and analysis. The control samples were prepared and run at a later date while the unknown group

PLATE 1 I.R.-AMINE ABSOPRTION
HEXYLAMINE IN CCl_4

(C = 3.125%;%T = 52%)



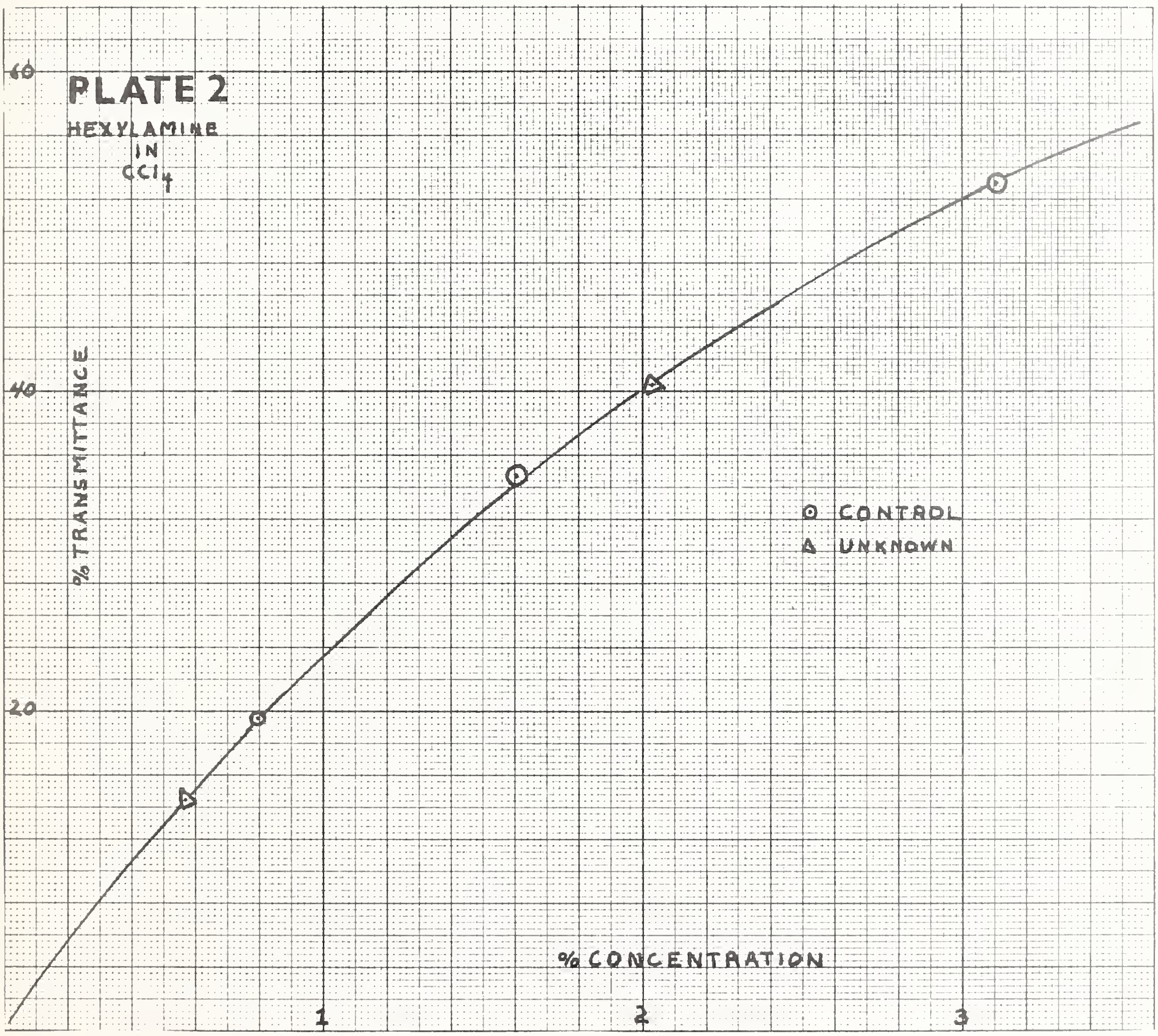
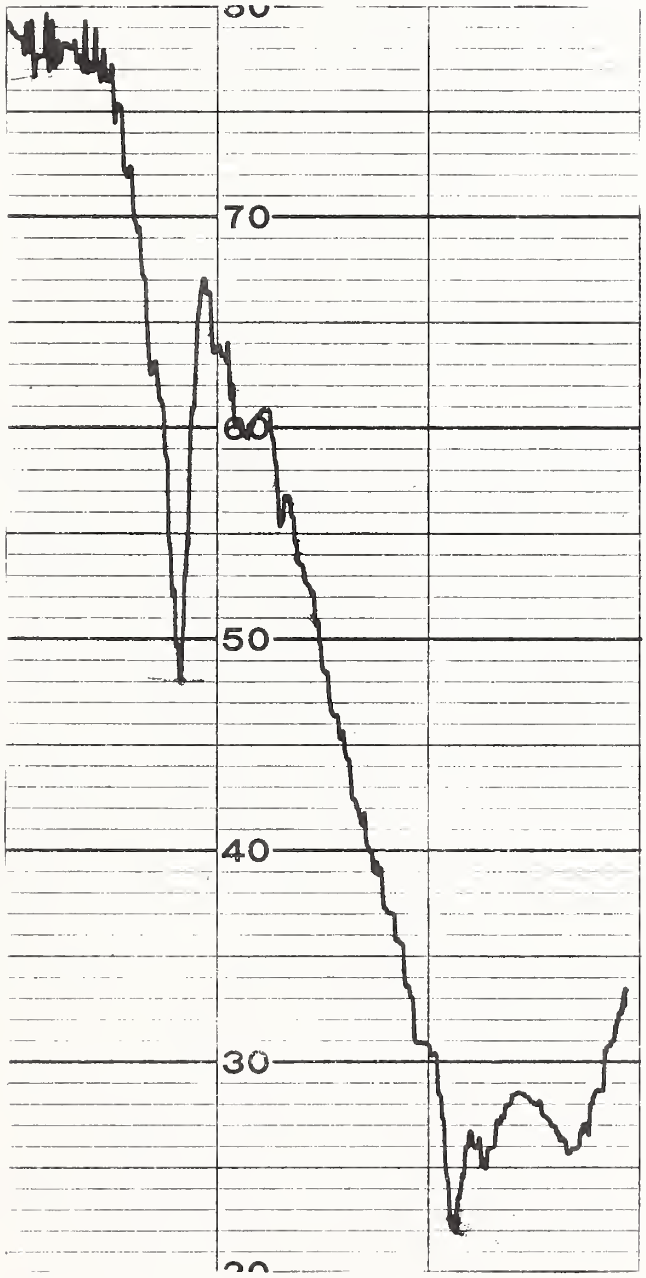


PLATE 2
HEXYLAMINE
IN
CCl_4
60
40
20
% TRANSMITTANCE
⊙ CONTROL
△ UNKNOWN
% CONCENTRATION
1
2
3

was prepared and run immediately. Since the unknown group gave a high reading a chemical reaction was suspected within the standards. This assumption was confirmed when a compound was extracted from the solutions in small quantites. It was a solid material soluble in dilute hydrochloric acid but insoluble in carbon tetrachloride, acetone or water. It was purified by washing in carbon tetrachloride and acetone and possessed a sharp melting point at 278° C. A spectra was obtained from a KBr wafer. This and a mixed melting point eliminated the possibility of aniline hydrochloride. Interpretation of the spectra indicated that the unknown belonged in the acredine family and that there is an attached chlorine and an attached primary amine. The Sadtler Index did not contain a spectra for a chloro amino acredine. The material proved to be soluble in diphenylamine and a molecular weight of 204 was calculated from its freezing point depression. The straight line obtained for the standards indicates that the reaction kinetics are first order.

A mixture of arosurf AA-11 and carbon tetrachloride was prepared for determination of the arosurf. Since this is an approved adhesive agent, extending the procedure to cover small concentrations in asphalt was anticipated. An absorption band at 3800 wave numbers was chosen as there is no corresponding band in asphalt. An unknown of 1.75% was correctly evaluated and yielded a percent transmittance of 24% with the 3mm path length. Some stability problems were encountered with the instrument. Immediately prior to the determination the chopper motors had been turned off. This shut-down time was approximately $1\frac{1}{2}$ hours. When the spectra was run immediately after turning the motors on the sample evaluated at 1.4%. A re-run 15 minutes later yielded the correct result. This represents a 25% increase over the 15 minute period. It is apparently necessary that the glower be in full operation for at least one-half hour prior to an analysis. Since field samples will be in the neighborhood of 1% additive concentration standards were prepared at .333%, .20%

PLATE 3 I.R.-AMINE ABSORPTION
AROSURF AA-11 IN CCl_4
(C= 2%;%T= 31.5%)



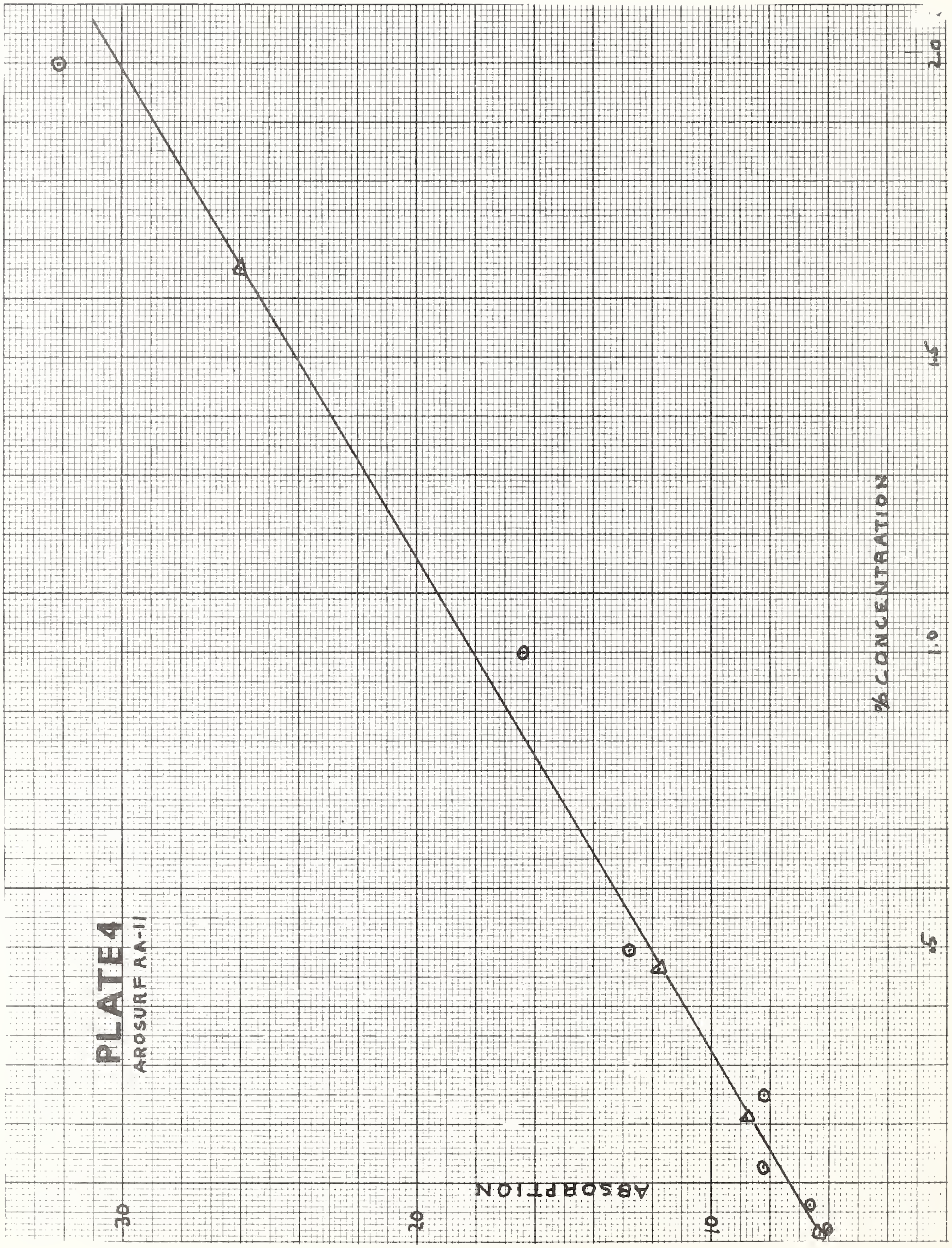


PLATE 4
AROSURF AA-11
% CONCENTRATION
ABSORPTION
30
20
10
.5
1.0
1.5
2.0

and .077%. The 3mm cell was again used. These were analyzed as .46%, .21% and .015%. The accuracy of the 2% sample is considered coincidental. The 3mm cell gave percent transmittance values in the neighborhood of 10% with an instrumental noise level of 2% and the readability of the chart was limited. The error can be attributed to too small a sample thickness. A sample path of about 25 mm would yield a percent transmittance of 80% which would yield maximum accuracy. Since there is no energy loss incurred by this increase in path length, percent concentrations of under one-half percent may be accurately determined. The Barnes Instrument Corporation now produces variable path cells of up to 50 mm length which would be adequate to .007%.

Low Concentration Studies

Fixed path gas cells of 10 mm, 25 mm, and 50 mm were obtained. Solutions of benzene in carbon tetrachloride were made in the concentration range from .07 to .004 percent. These were run on the I. R. and the absorption spectra was recorded. A similar procedure was followed for aniline, with the added precaution of running the spectra as soon as the samples were mixed. From these curves, the concentration of an unknown was easily determined in the low concentration range, and the absorption proved to be linear.

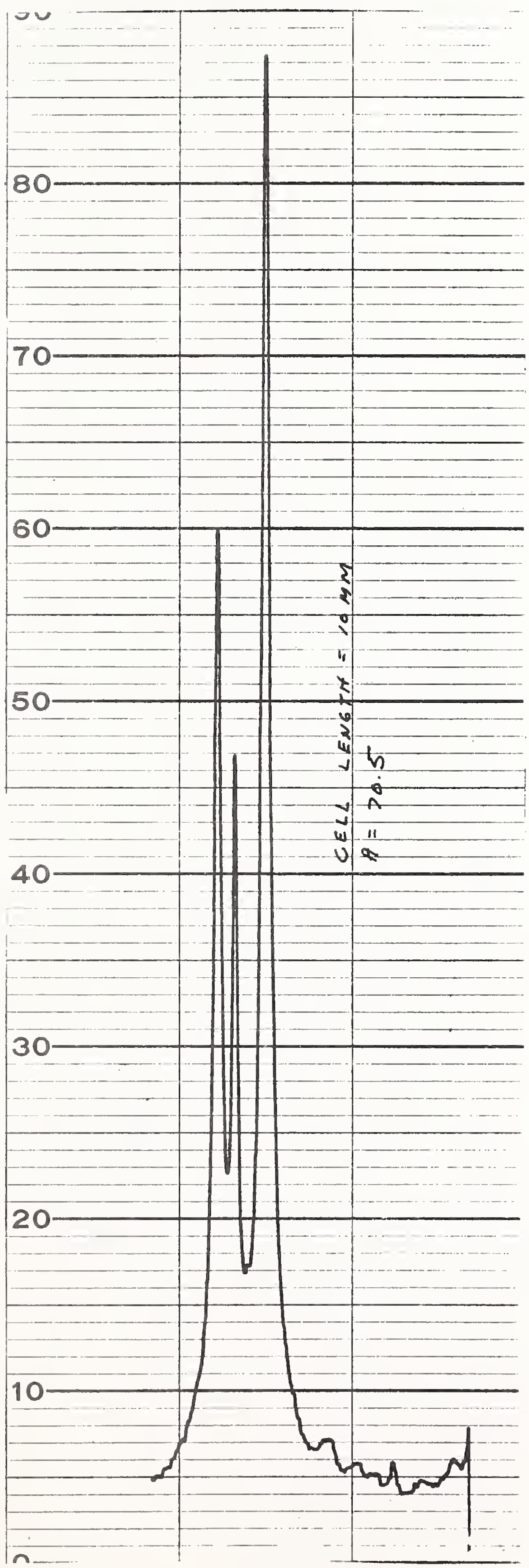
Dilutions were made of a Phillips 100-200 asphalt with carbon tetrachloride. The asphaltic amine peaks were measurable semiquantitatively and the addition of aniline was discernable. Dilution techniques with asphalt seem to be the biggest problem in obtaining completely quantitative procedures. Some of the dilutions fell on the prescribed line but others did not.

Tables I-III show the tabulated data for the benzene control. Plate 5 shows the pertinent benzene spectra while Plates 6-8 show absorption as a function of concentration for the three cells. Plate 9 shows the aniline spectra while Plates 10-13 show absorption as a function of concentration.

Conclusions

Quantitative determinations can be obtained with infrared analysis in the range of .005% or less with suitable cells. The Beer-Lambert Law is entirely valid in this range. In order to determine the quantity of an adhesive agent in asphalt it would be best to have samples of the agents to use as standards. It is not possible to identify a particular agent by spectra alone.

PLATE 5 BENZENE ABSORPTION



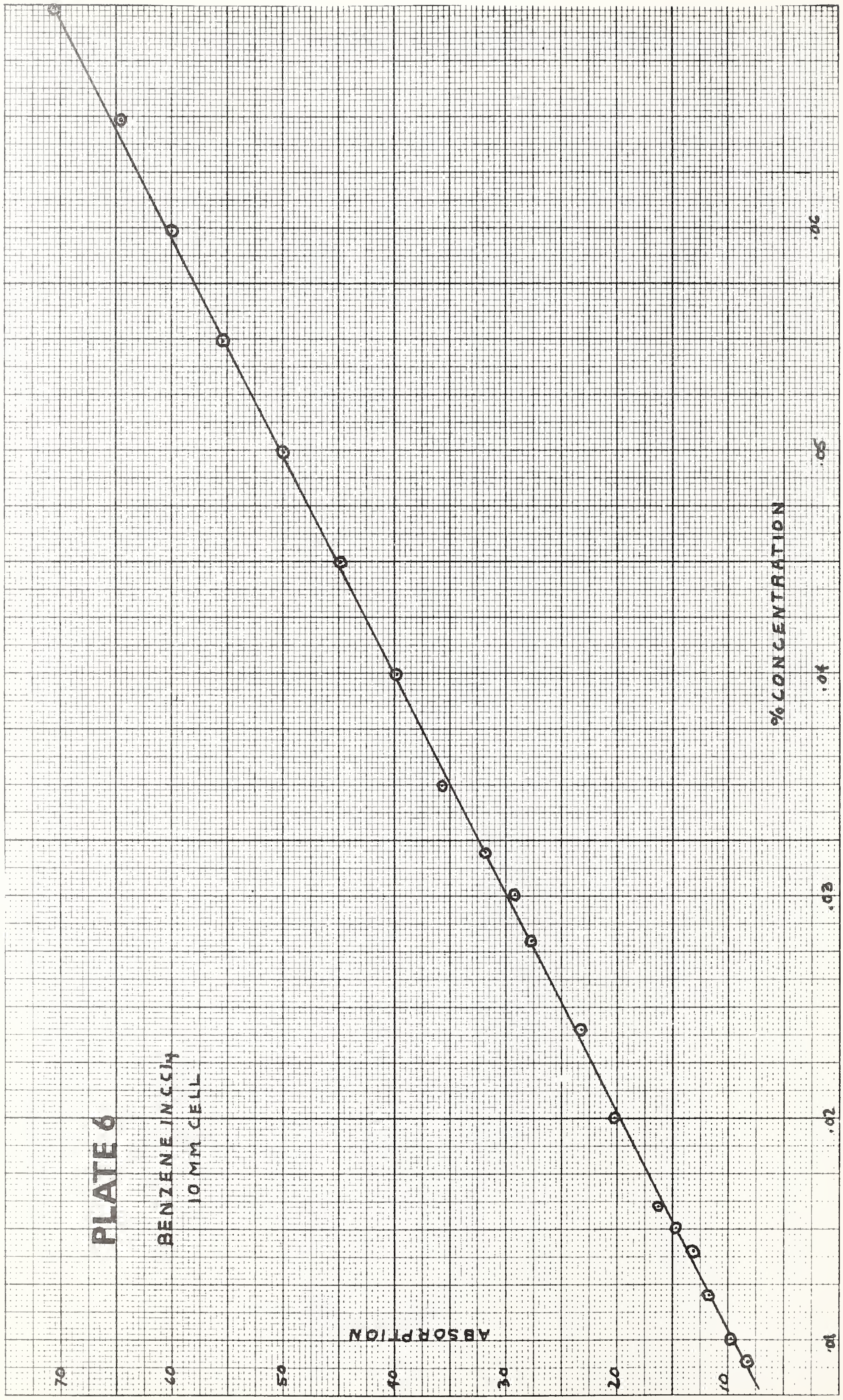


PLATE 6
BENZENE IN CCl4
10 MM CELL
ABSORPTION
% CONCENTRATION
10
20
30
40
50
60
70
.01
.02
.03
.04
.05
.06

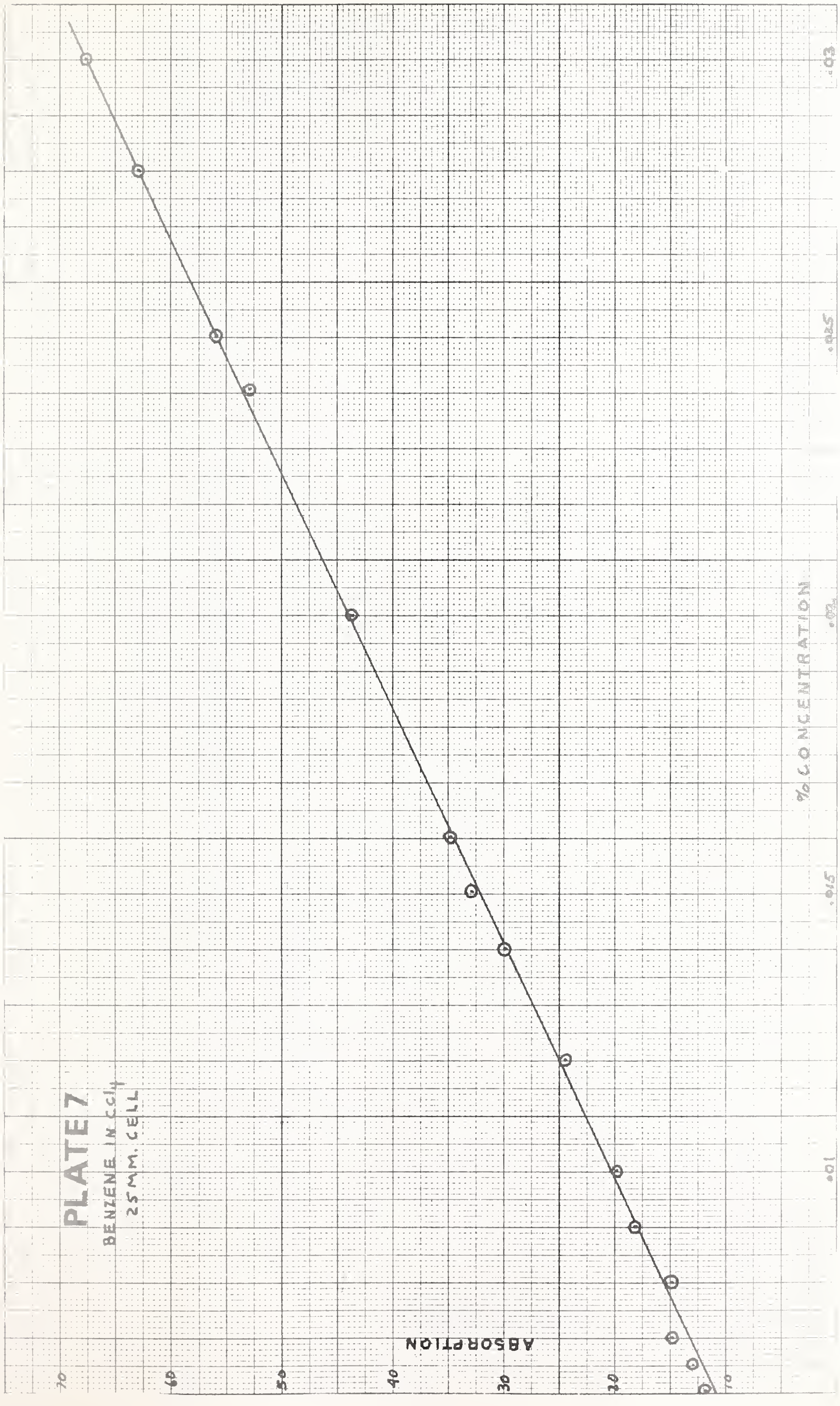


PLATE 7
BENZENE IN CCl_4
25 MM. CELL
% CONCENTRATION
ABSORPTION
.01
.015
.02
.025
.03
10
20
30
40
50
60
70

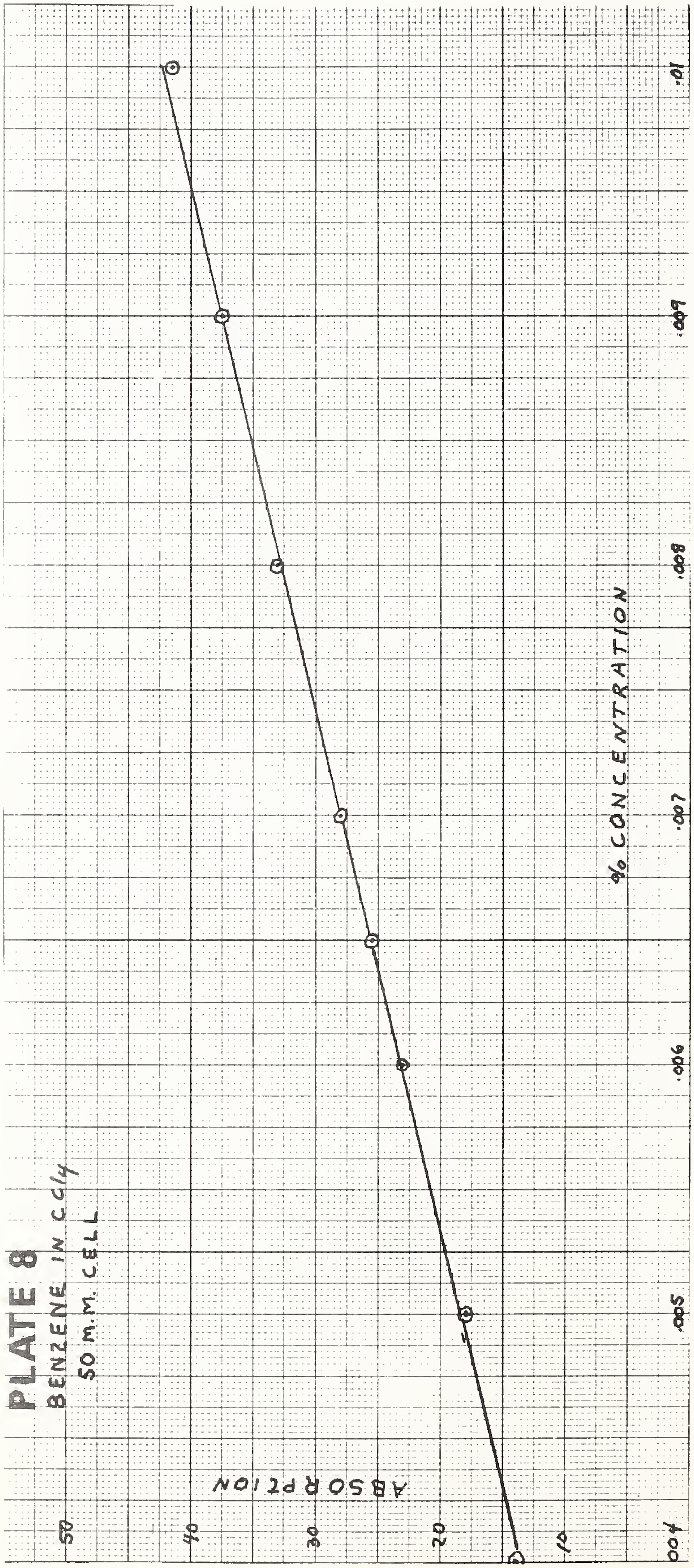
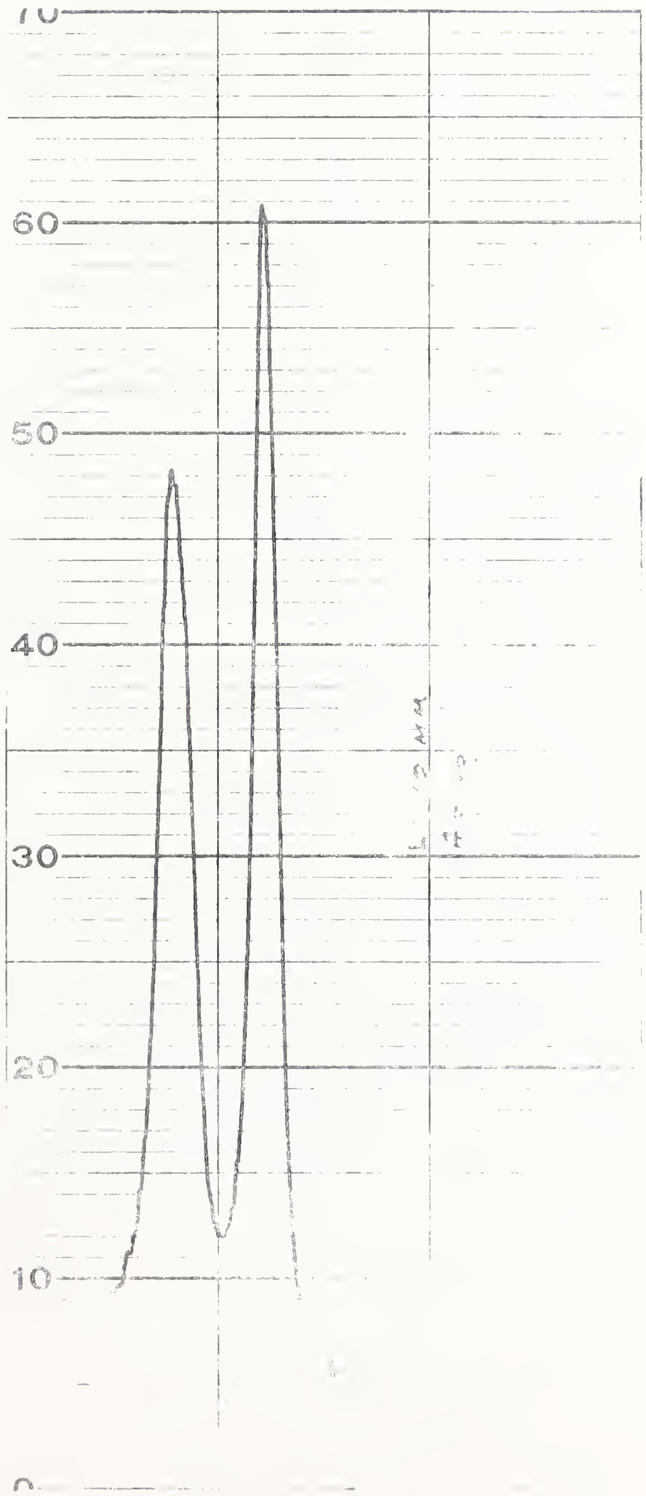


PLATE 8
BENZENE IN CCl_4
50 M.M. CELL
ABSORPTION
% CONCENTRATION
50
40
30
20
10
.004
.005
.006
.007
.008
.009
.01

PLATE 9 I.R.-AMINE ABSORPTION
ANILINE IN CCl_4



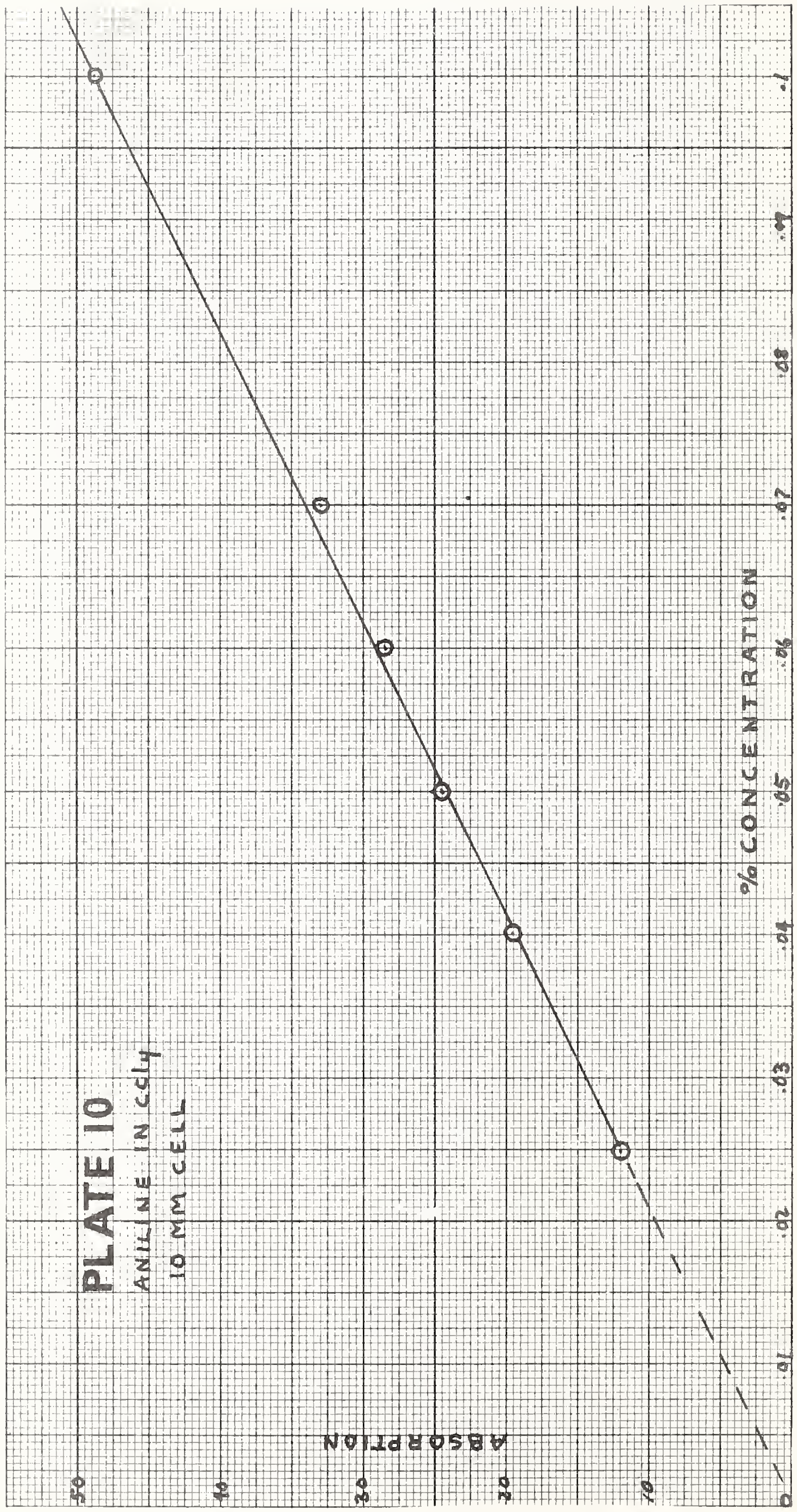


PLATE 10
ANILINE IN CCl4
10 MM CELL
% CONCENTRATION
ABSORPTION
0
10
20
30
40
50
.01
.02
.03
.04
.05
.06
.07
.08
.09
.1

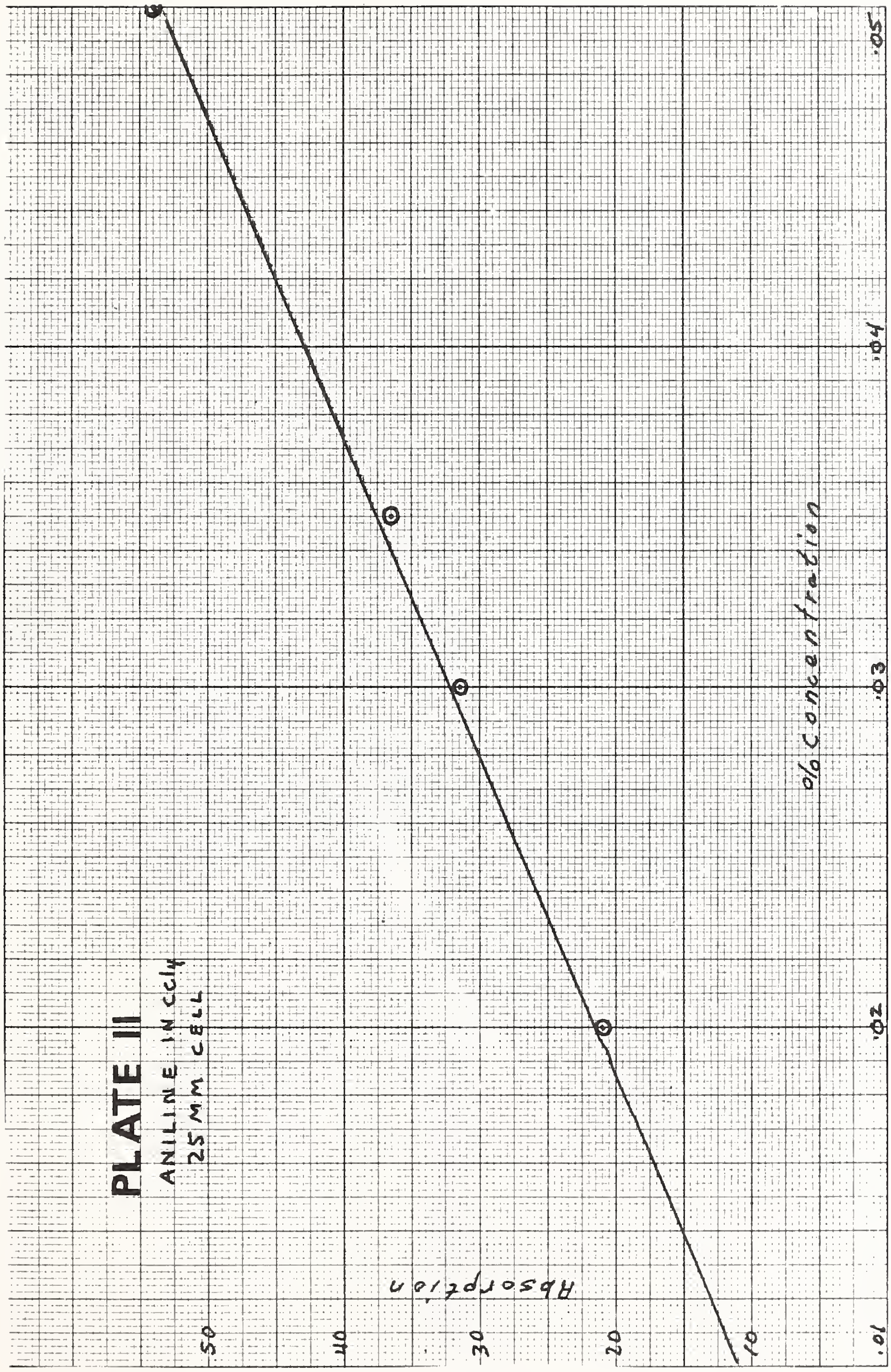


PLATE II
ANILINE IN CCl_4
25 MM CELL
Absorption
% Concentration
.01
.02
.03
.04
.05
10
20
30
40
50

PLATE 12
ABSORPTION VS CONCENTRATION
ANILINE
50mm. CELL

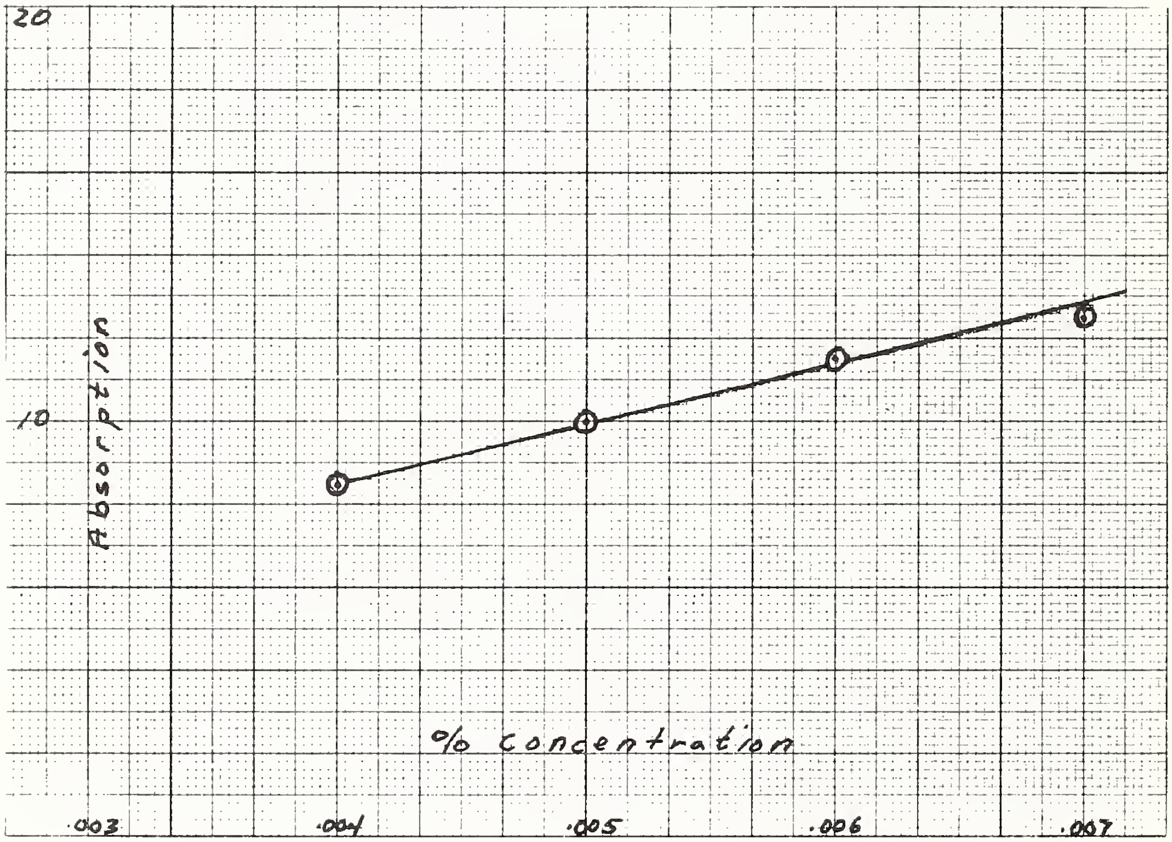


TABLE I

BENZENE

TABULATION FOR 10 mm. CELL

SAMPLE NUMBER	% CONCENTRATION	ABSORPTION
1	.070	70.5
8	.065	64.5
2	.060	60
10	.055	55.5
3	.050	50
11	.045	45
4	.040	40
12	.035	36
17	.032	32
3	.030	29.5
20	.028	28
23	.024	23.5
13	.020	20.5
18	.016	16.5
14	.015	15
21	.014	13.5
24	.012	12
15	.010	10
16	.009	8.5

TABLE II

TABULATION FOR 25 mm. CELL

17	.032	73
5	.030	68
20	.028	63
7	.025	56
23	.024	53
13	.020	44
18	.016	34.5
14	.015	33
21	.014	30
24	.012	24.5
6	.010	20
16	.009	18.5
19	.008	16.5
22	.007	15
9	.0065	13
25	.0060	12

TABLE III

TABULATION FOR 50 mm. CELL

SAMPLE NUMBER	% CONCENTRATION	ABSORPTION
6	.01	41.5
16	.009	37.5
19	.008	33
22	.007	28
9	.0065	25.5
25	.006	23
26	.005	18
27	.004	14

PART I-E

APPENDIX

List of Available Spectra

The following is a list of spectra which were run and are on file together with the sample preparation data.

High Resolution Studies

High resolution spectra were made on an SC-250 and an MC-800 Asphalt as well as on an oleic acid sample. These were completed with the idea of trying to calculate the hydrogen bonding interaction energy in the appropriate asphalts from frequency shifts for the different functional groups. In polymeric systems, a frequency shift occurs which is directly proportional to the hydrogen bonding in the system. This is called the Badger rule and is discussed in the books on hydrogen bonding. Through appropriate calculations it should be possible to determine which groups take part in the actual crosslinking within the asphalt, and to obtain another independent value for the average hydrogen bonding energy. No attempt was made to complete these calculations but they should be tedious rather than difficult.

	SAMPLE NAME	TYPE OF SAMPLE	NOTES	DATE SAMPLE PREPARED
	KBr	Contaminated KBr using 94 Pen asphalt 0.4 gram	KBr was contaminated by placing KBr and asphalt in oven	3-20-64 A.M.
	KBr	Pure KBr undried 0.4 gram	Reagent grade KBr	3-20-64 A.M.
	KBr	Pure KBr dried 0.4 gram	Reagent grade KBr oven dried - $2\frac{1}{2}$ hours temp. unknown	3-20-64 A.M.
	KBr	Pure KBr dry 0.4 gram		
	KBr .4 gram Sample	Pure KBr, Dry	Matched pellets for double beam concel-lation of KBr. Obtain high resolution at slow speed	
MATCHED	KBr .4 gr. Asphaltenes of absorp-tion separa-tion .001 gm.	Pure KBr, Dry + .001 gm. of asphalt-ene	CH_3:CH_2 ratio 1 2900 cm branching 1350 to 1450	
	KBr .2 gram	Pure KBr, Dry	After pellet is made weigh	3-23-64
	KBr .2 gram	Pure KBr, Dry	Before making pellet and after grinding dry in vacuum oven	3-23-64
	KCL .2 gram	Pure KCL, Dry	Dry before making pellet	3-23-64
	KBr .4 gram	KBr plus asphalt unknown	.4 g KBr .005 gr. unknown Make 1 .4 gr.pellet	3-24-64

SAMPLE NAME	TYPE OF SAMPLE	NOTES	SAMPLE PREPARED
226542	Aggregate KBr	.0005 gr. .4000 gr.	Run 3-25-64 Mar. 24
221684	Aggregate KBr	.0005 gr. .4000 gr.	Mar. 24
227257	Aggregate KBr	.0005 gr. .4000 gr.	Mar. 24
227516	Aggregate KBr	.0005 gr. .4000 gr.	Mar. 24
228305	Aggregate KBr	.0005 gr. .4000 gr.	Run 3-27-64 Mar. 22
222392	Aggregate KBr	.0005 gr. .4000 gr.	Mar. 25
240089	Aggregate KBr	.0005 gr. .4000 gr.	Mar. 25
227840	Aggregate KBr	.0005 gr. .4000 gr.	Mar. 25
Asphaltenes n-pentane 84 Pen	Asphaltenes KBr	.0005 gr. .4000 gr.	Mar. 25
Oils from Phillips 84 Pen n-pentane	Slide thin No solvent		Mar. 25
Asphalteen 84 Pen	KBr Asphalteen	.4 gram .002 gram	3-26-64 Run 3-26-64

SAMPLE NAME	TYPE OF SAMPLE	NOTES	SAMPLE PREPARED
Saran Sheets	Mount a saran untreated sheet in a card board	Sample size should be approximately the same size as a polystyrine	3-31-64
Ammonium Stearate	Ammonium Stearate KBr	.0005 gr. .4 gr. Dry stearate for 1 hr. 250° on hot plate	
Thiourea	Thiourea KBr	.0005 gr. .4 gr. Dry thiourea for 2 hr. in 220°	
Lab. # 286114 Test # 4888 Quartzite	Aggregate KBr	.0005 gr. .4 gr. Dry sample 12 hrs. 220°	Mar. 26
226542	Aggregate KBr	.002 gr. .4 gr.	Mar. 30
221684	Aggregate KBr	.002 gr. .4 gr.	Mar. 30
227257	Aggregate KBr	.002 gr. .4 gr.	Mar. 30
227516	Aggregate KBr	.002 gr. .4 gr.	Mar. 30
228305	Aggregate KBr	.002 gr. .4 gr.	Mar. 30
222392	Aggregate KBr	.002 gr. .4 gr.	Mar. 30
240089	Aggregate KBr	.002 gr. .4 gr.	Mar. 30

SAMPLE NAME	TYPE OF SAMPLE	NOTES	SAMPLE PREPARED
227840	Aggregate KBr	.002 gram .4 gram	Mar. 31
Cyclics from Phillips 84 Pen	Slurry	Thin	Run Mar. 31
Oils from Phillips 84 Pen n-pentane	Slurry	Thin	
Saturates from Phillips 84 Pen	Slurry	Thin	
Dodecane 1:10	Liquid Cell		Run 3-31-64
Acrylic Acid 1:10	Liquid Cell		Run 3-31-64
6 notonic Acid	Liquid Cell		Run 3-31-64
KBr absor-bed Asphalt MC-800 0 tó 130^{o} F #1	KBr Pellet	.4 gm. of already mixed sample	
KBr absor-bed Asphalt MC-800 130 to 160^{o} F #2	KBr Pellet	.4 gm. of already mixed sample	Run 4-1-64
KBr absorb-ed Asphalt MC-800 160 to 190^{o} F #3	KBr Pellet	Agm of already mixed sample	Run 4-1-64
KBr absorb-ed Asphalt MC-800 #4 190 to 226^{o} F	KBr Pellet	Agm of already mixed sample	Run 4-1-64

SAMPLE NAME	TYPE OF SAMPLE	NOTES	SAMPLE PREPARED
KBr absorb-ed Asphalt MC-800 #5 226 to 260° F	KBr Pellet	Agm of already mixed sample	Run 4-1-64
KBr absorb-ed Asphalt MC-800 #1 to 130°F	KBr Pellet	3 parts plain KBr 1 part absorbing KBr .4 am total sample	
Kerosene	Liquid Cell .025 mm. spacer	Kerosene in cold room	
Dodosane 1:10	Liquid Cell .025 mm. spacer		Run 4-2-64
Phillips 84 Pen	Slurry		Run 4-2-64
Naptha X	Liquid Cell .025 mm. spacer	Approx. 1 cc.	Run 4-2-64
Naptha Y	Liquid Cell .025 spacer	Approx. 1 cc.	Run 4-2-64
Oizan A	.0005 gram .4 gr. KBr		4-2-64
Kerosene	Liquid Cell .025 mm. sporer	Approx. 1 cc.	Run 4-2-64
Naptha	Liquid Cell No sporer	Approx. 1 cc.	Run 4-3-64
Naptha	Liquid Cell No sporer	Approx. 1 cc.	Run 4-3-64

SAMPLE NAME	TYPE OF SAMPLE	NOTES	DATE SAMPLE PREPARED
Oizan A	.002 gram .4 KBr		4-2-64
Ozian A	.001 gram .4 gr. KBr		4-2-64
Oizan S	.005 gram .4 gr. KBr		4-2-64
Kerosene	Liquid Cell No sporer Not sufficient	Approx. 1 cc.	Run 4-3-64
Kerosene	Liquid Cell .025 Sporer	Approx. 1 cc.	Run 4-3-64
Brominated Phillips 84 Pen	Slurry	Small amount of CCl_4 used	Run 4-3-64
Oizan S	.001 gram .4 gr. KBr		4-3-64
Phillips 84 Pen	KBr Pellet	130°F .351	4-13-64
Phillips 84 Pen	KBr Pellet	140°F .4 gram	4-13-64
Phillips 84 Pen	KBr Pellet	150°F .4 gram	4-13-64
Phillips 84 Pen	KBr Pellet	160°F .4 gram	4-13-64

SAMPLE NAME	TYPE OF SAMPLE	NOTES	DATE SAMPLE PREPARED
Phillips 84 Pen	KBr Pellet	180°F .4 gram	4-13-64
Phillips 84 Pen	KBr Pellet	190°F .386 grams	4-10-64
Phillips 84 Pen	KBr Pellet	200°F .265 grams	4-10-64
Phillips 84 Pen	KBr Pellet	210°F .386 grams	4-10-64
Phillips 84 Pen	KBr Pellet	220°F .4 grams	4-10-64
Phillips 84 Pen	KBr Pellet	230°F .306 grams	4-10-64
Phillips 84 Pen	KBr Pellet	240°F .4 gram	4-10-64
Mexican 70 Pen Saturate 4-10-64	Slurry Thick		Pen 4-13-64
Mexican 70 Pen Saturates 4-10-64	Slurry Thin		Pen 4-13-64
Brominated Mexican Asphalt	KBr .5 gram Asphalt .002 gram	Pellet	4-13-64
Mexican Asphaltenes 4-3-64	KBr .5 gram Asphalt .002 gram	Pellet	4-13-64

SAMPLE NAME	TYPE OF SAMPLE	NOTES	DATE SAMPLE PREPARED
Mexican 70 Pen Asphaltene Asphaltics REsin	KBr .5 gram Asphaltene & Resins .002 gr.	Pellet	4-13-64
Ash Mexican 70 Pen	KBr .5 gram Ash 1 mg.	Pellet	4-14-64
Salts sample brought in by hi-school boy	.002 gram sample .4 gram KBr	Pellet	4-14-64
Oils from Phillips 84 Pen removed by N-Pentane 4-13-64	Thick and Thin	Slurry	4-13-64
Mexican Pen 70 Cyclics April 10, 64	Slurry		4-13-64
Mexican 70 Pen Resins 4-6-64	Slurry		4-14-64
Mexican 70 Pen Petrolenes 4-13-64	Slurry		4-14-64
Cyclics from Phillip 84 Pen 3-30-64	Slurry Thick	difficult, must be heated approx. 4-5 low heat.	4-15-64
Oils from Mex. 70 Pen 4-1-64	NaCL, plate	spaces must be used - MTL is too soft for slurry type.	Run 4-15-64
Cyclics from Phillips 84 Pen 3-30-64	Plate	Spacer	4-16-64
Saturates Phillips 84 Pen 3-30-64	Plate		4-16-64

SAMPLE NAME	TYPE OF SAMPLE	NOTES	DATE SAMPLE PREPARED
Phillips 84 Pen Asphalt Res. 4-17-64	Slurry Plate		Run 4-17-64
Diamond Saturates 107 Pen	Slide		Run 4-20-64
Diamond 107 Pen Cyclics	Slide		Run 4-20-64
Diamond 107 Pen Petrolene	Slide		Run 4-20-64
Diamond 104 Pen Pine As-phalt	Slide		Run 4-20-64
Diamond 107 Pen Asphaltene			
4-17-64 Asphaltene from Diamond 107 Pen	Pellet	.002 Sample .4 gr. KBr	4-21-64
4-24-64 96 Pen Farmers Saturates	Slide	Thick samples	Run 4-24-64
4-24-64 96 Pen Farmers Saturates	Slide	Thin	Run 4-24-64
4-24-64 96 Pen Farmers Cyclics	Slide	Thick sample	Run 4-24-64
4-24-64 96 Pen Farmers	Slide	Thick samples	Run 4-24-64

SAMPLE NAME	TYPE OF SAMPLE	NOTES	DATE SAMPLE PREPARED
107 Diamond Ester?	greenish gray wax Diamond 107	dissolved in CCl_4 dried with N_2 no spacer	Run 4-27-64
107 Diamond Ester?	Light brown wax Diamond 107	dissolved in CCl_4 dried with N_2 No spacer	Run 4-27-64
107 Diamond Ester?	Brown oil Diamond 107	removed from H_2O dissolved in CCl_4 dried with N_2 No spacer	Run 4-27-64
Farmers 96 Pen Petrolenes	Slurry	must be heated to be used.	Run 4-27-64
Farmers 96 Pen Asphaltene	Flakes	must be dissolved in CCl_4.	4-27-64
Diamond Sc_2 50 Oils from Ester	Slurry	watch for H_2O must be handled carefully	Run 4-27-64
Farmers 96 Pen Asphaltene	Pellet	.002 Samples .4 KBr	Run 4-28-64
Armour Ethomer C/25 hot 7080	Slurry		Run 4-29-64
Phillip Con/Blen Anti slip #2	Slurry		Run 5-1-64
Esterification of di-cam 107 alchol Hg NOG CCl_4	Slurry		Run 5-4-64
4-27-64 Asphaltenes N-Pentane Conoco 102 Pen	Pellet	.4 gm KBr .002 Samples	Run 5-4-64

SAMPLE NAME	TYPE OF SAMPLE	NOTES	DATE SAMPLE PREPARED
Conoco 102 Pen Asphalt	Slurry	very thick and difficult to use must be heated	Run 5-4-64
Conoco 102 Pen Petrolene	Slurry	must be heated slightly	Run 5-5-64
Conoco 102 Pen Cyclics 4-30-64	Slurry	must be heated slightly	Run 5-5-64
Acid Board of Health	Slurry	dissolve in CCl_4	5-5-64
Conoco 102 Pen Saturate	Slide		Run 5-5-64
Conoco Flex Oil 5-5-64	Slide Film	use when thin films are required	Run 5-5-64
Oxides of metals from conoco cycle stack	Pellet	.03 gr. sample .4 g KBr	5-14-64
Big West 96 Pen Asphaltenes	Pellet	.02 gr. asphaltine .4 KBr	5-14-64
Big West Whole asphalt	Slide		5-14-64
Big West Cyclics	Slide		5-14-64
Big West Asphaltics	Slide		5-14-64

SAMPLE NAME	TYPE OF SAMPLE	NOTES	DATE SAMPLE PREPARED
Big West Petrotenes	Slide		5-14-64
Big West Saturates	Slide		5-14-64
Farmers Humble oils from cyclics 150-200 Pen	Slide	must be heated slightly	Run 5-21-64
Cyclics in resins Mex. 70 Pen	Slide		
Saturates in Resin for Mex. Pen 70	Slurry	Had to be dissolved in CCl_4 Slide is prepared as in des.	Run 6-3-64
Saturates in oils from Mex. 70 Pen 5-28-64	Slide	Easy to work with	6-3-64
Nat'l Aluminate Corp. #1	Slide	Easy to work with	6-12-64
Armour Redicote 75 9.	Slide	Easy to work with	6-12-64
Conoco Blend of 97 Pen Oils from thin film 6-3-64	Slide	Easy to work with	Run 6-15-64
Cyclics Conoco Thin Film Flux Oil	Slide	Easy to work with	Run 6-16-64
Cyclics from conoco cycle stock	Slide	Easy to work with	Run 6-16-64
Saturates in the oils from Mex. of 70 Pen May 28, '64	Slide	.25 Spacer used	Run 6-17-64

SAMPLE NAME	TYPE OF SAMPLE	NOTES	DATE SAMPLE PREPARED
Saturates Conoco Thin film Flux oil	Slide	Easy to work with	Run 6-17-64
Cyclics in resins from Mex. 70 Pen	Slide	hard to work	Run 6-17-64
Cyclics in oils from Mex. 70 Pen 5-28-64	Slide	Easy to work with	Run 6-19-64
June 30, 1964 Cyclics composite of Farmers 100-120 pen 23%	Slide	Very hard to work with, must be warmed	7-10-64
Asphaltics June 29, 1964 Composite of Farmers 100-120 pen 27%	Slurry	Hard to work with. CCl_4 Solvent	Run 7-10-64
Saturates 6-30-64 Comp. of Farmers 100-120 pen 51%	Slide	Must be warmed Hard to work with.	Run 7-9-64
Whole asphalt Farmers comp. 100-120 pen	Slide	Hard to work with must be warmed	7-9-64
Cyclics 20% 7-9-64 Comp. of Phillips 100-120 Pen	Slide	Hard to work with	Run 7-10-64
Saturates Comp. of Phillips 100-120 pen 45%	Slide	Easy to work with.	Run 7-14-64
Saturates 28% Big West 110 Sample from stream by Westvelt	Slide		Run 7-13-64
Whole Asphalt Phillips Composite of 100-120 Pen	Slide		Run 7-13-64

SAMPLE NAME	TYPE OF SAMPLE	NOTES	DATE SAMPLE PREPARED
Asphaltics Phillips 35% Composite of 100-120 Pen	Slurry	Hard to work with. CCl_4 Solvent	Run 7-14-64
Cyclics 46% Big West 110 Sample from stream by Westvelt	Slide	Easy to work with on the first run. Difficult on the last run.	Run 7-15-64
Saturates ores from Farmers Humble 150-200 Pen	Slide	Easy to work with	Run 6-19-64
Armour 3 - redi-cote 75+X Fatty ni-trogen derv	Slide	Easy to work with	Run 6-22-64
Hercules Amino - D. HM - 92	Slide	if warmed slightly, it has a better con	Run 6-22-64
Phillips Com L Blend Anti-stays #2 2	Slide	Easy to work with	Run 6-22-64
June 15, 64 Cyclics Composite of Conoco 100-120	Slide	Easy to work	Run 6-22-64
June 15, 64 Saturates Composite of Conoco 100-120	Slide	Thick material rather difficult to use	Run 6-23-64
June 3, 64 Cyclics Conoco thin Film blend 97 Pen sol-vent methol	Slide	must be heated slightly	Run 6-23-64
Maguire Nostrip Acra 300-8	Slide	Sticky and diffi-cult to work with	Run 6-23-64
Diamond Whole Asphalt	Slide	Hard to work with. Needs to be heated.	Run 7-28-64

SAMPLE NAME	TYPE OF SAMPLE	NOTES	DATE SAMPLE PREPARED
Diamond Asphaltics Composite 100-120 35%	Slurry	CCl_4 Driven out with infra-red heat lamp.	Run 7-28-64
Cyclics Conoco 38% 6-15-64 100-120 pen	Slide	Easy to work with	Run 7-28-64
Saturates Composite 23% 100-120 pen Conoco	Slide	Easy to work with.	Run 7-28-64
Asphaltics Conoco 38% Comp. of 100-120 pen	Slurry	Dried with infra-red lamp.	Run 7-29-64
Whole Asphalt Conoco Comp. 100-120 pen	Slide	Hard to work with. Must be heated.	Run 7-29-64
Big West 110 Whole Asphalt	Slide	Hard to work with.	Run 7-15-64
Big West Cyclics July 8, 64 46%	Slide	Easy to work with at first, but difficult to thin.	Run 7-17-64
Humble 47% Saturates Comp. 100-120 pen July 6, 64	Slide	Easy to work with.	Run 7-20-64
Humble 20% Cyclics Comp. 100-120 Pen	Slide	Difficult to work with.	Run 7-20-64
Humble Whole Asphalt Comp. 100-120 pen	Slide	Difficult to work with.	Run 7-20-64
Big West Cyclics 110 Sample from stream by Westvelt	Slide	Easy to work at first, but very difficult to thin.	Run 7-21-64

SAMPLE NAME	TYPE OF SAMPLE	NOTES	DATE SAMPLE PREPARED
Humble 34% Asphaltics Comp. of 100-120 Pen	Slurry	CCl_4 driven off by infra-red lamp.	Run 7-21-64
Big West Asphaltics 26%	Slurry	CCl_4 driven off by infra-red lamp.	Run 7-21-64
Cyclics 26% Diamond Comp. 100-120 June 19, 1964	Slide	Easy to work with.	Run 7-28-64
Saturates 40% Diamond Comp. 100-120 6-19-64	Slide	Easy to work with.	Run 7-28-64
Big West MC-800 Lab 285711	Slide	Easy to work	8-27-64
Distillation Residue from Phillips MC-800 1295 84.5% Volume	Slide	Easy to work	8-28-64
Overhead From Distillation of Phillips MC-800 15.5% by Volume	Liquid Cell	.025 spacer Easy to work	8-28-64
Humble SC-250 Field 21287	Slide	.025 spacer	8-31-64
Diamond SC-800 1964	Slide	Easy to work	8-31-64
Diamond SC-800 Field 929	Slide	Easy to work	9-2-64
Conoco SC-250 1964	Slide	Easy to work	9-3-64

SAMPLE NAME	TYPE OF SAMPLE	NOTES	DATE SAMPLE PREPARED
Farmers SC-800 11305	Slide	Easy to work	9-8-64
Big West SC-800 1964	Slide	Easy to work	9-9-64
Diamond SC-250 1963	Slide	Easy to work	9-9-64
Diamond MC-300 #959	Slide	Easy to work	
Farmers SC-250 11304	Slide	Easy to work	
Big West SC-250 Lab. #291945	Slide	Easy to work with	Run 8-14-64
Humble SC-800 21343	Slide	Easy to work with.	Run 8-14-64
Farmers SC-800 Lab. 293107	Slide	Easy to work with.	Run 8-14-64
Big West SC-800 Lab. 293107	Slide	Easy to work with.	Run 8-17-64
Farmers SC-800 Lab. 11324	Slide	Easy to work with.	Run 8-17-64
Farmers RC-250 #11316	Slide	Easy to work with.	Run 8-17-64

SAMPLE NAME	TYPE OF SAMPLE	NOTES	DATE SAMPLE PREPARED
Big West SC-800 With Nalco RL-1 Lab. #285716	Slide	Easy to work with	Run 8-17-64
Phillips SC-250 Field #6956	Slide-spacer-1st run	Easy to work with	Run 8-17-64
Diamond MC-3000 #957	Slide	Easy to work with	Run 8-18-64
Farmers SC-800 #1964	Slide	Easy to work with	Run 8-18-64
Farmers MC-800 Field #11234	Slide	Easy to work with	Run 8-18-64
Humble MC-800 Field #21345	Slide	Easy to work with	Run 8-19-64
Big West SC-800 with ½% Armour Lab. #285715	Slide	Easy to work	Run 8-11-64
Big West SC-250 Lab. #291012	Slide	Easy to work	Run 8-11-64
Big West SC-250 Lab. #293283	Slide	Easy to work	Run 8-11-64
Big West SC-250 Lab. #293109	Slide	Easy to work	Run 8-11-64
Big West MC-800 Lab. #293284	Slide	Easy to work	Run 8-12-64

SAMPLE NAME	TYPE OF SAMPLE	NOTES	DATE SAMPLE PREPARED
Big West SC-800 Lab. #293107	Slide	Easy to work	Run 8-12-64
Big West SC-800 Plain Lab. #285714	Slide	Easy to work	Run 8-12-64
Diamond MC-800 #985	Slide	Easy to work	Run 8-12-64
Conoco MC-800-A With Additive #985	Slide	Easy to work	Run 8-12-64
Big West SC-800 Lab. #291743	Slide	Easy to work	Run 8-14-64
Phillips SC-250 1963	Slide	Easy to work	Run 9-10-64
Conoco MC-800 #15686	Slide	Easy to work	Run 8-19-64
Phillips SC-800 Field #7106	Slide	Easy to work	Run 8-19-64
Conoco SC-800 #32989	Slide	Easy to work	Run 8-19-64
Conoco SC-800 Field #15673	Slide	Easy to work	Run 8-20-64
Phillips MC-800 Field #7065	Slide	Easy to work	Run 8-20-64

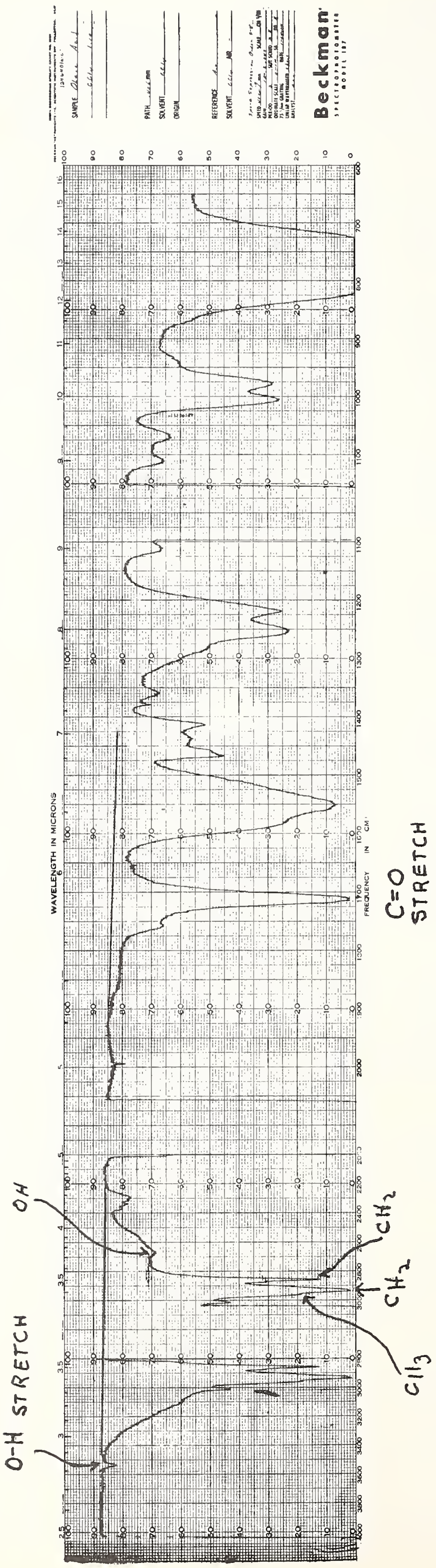
SAMPLE NAME	TYPE OF SAMPLE	NOTES	DATE SAMPLE PREPARED
Humble MC-800 1963	Slide	Easy to work	Run 8-20-64
Farmers MC-800 11243	Slide	Easy to work	Run 8-24-64
Humble RC-3 21319	Slide	Easy to work	8-24-64
Humble SC-800 7-6-64	Slide	Easy to work	8-24-64
Farmers SC-800 11275	Slide	Easy to work	8-25-64
Diamond SC-250 929	Slide	Easy to work	8-25-64
Farmers MC-800 11285	Slide	Easy to work	8-25-64
Humble MC-3 21310	Slide	Easy to work	8-27-64
Saturates 52% Farmers 100-120 Aged in air tight can for 11 mos.	Slide	Easy to work with	9-30-64
Saturates June 3, 64 - Conoco thin film - blend of 97 pen by solvent method	Slide	Easy to work with	10-1-64
Overhead (Diluent) from Distillation of Conoco MC-800 Amount 16%	Slide .025 spacer	Easy to work with	9-17-64

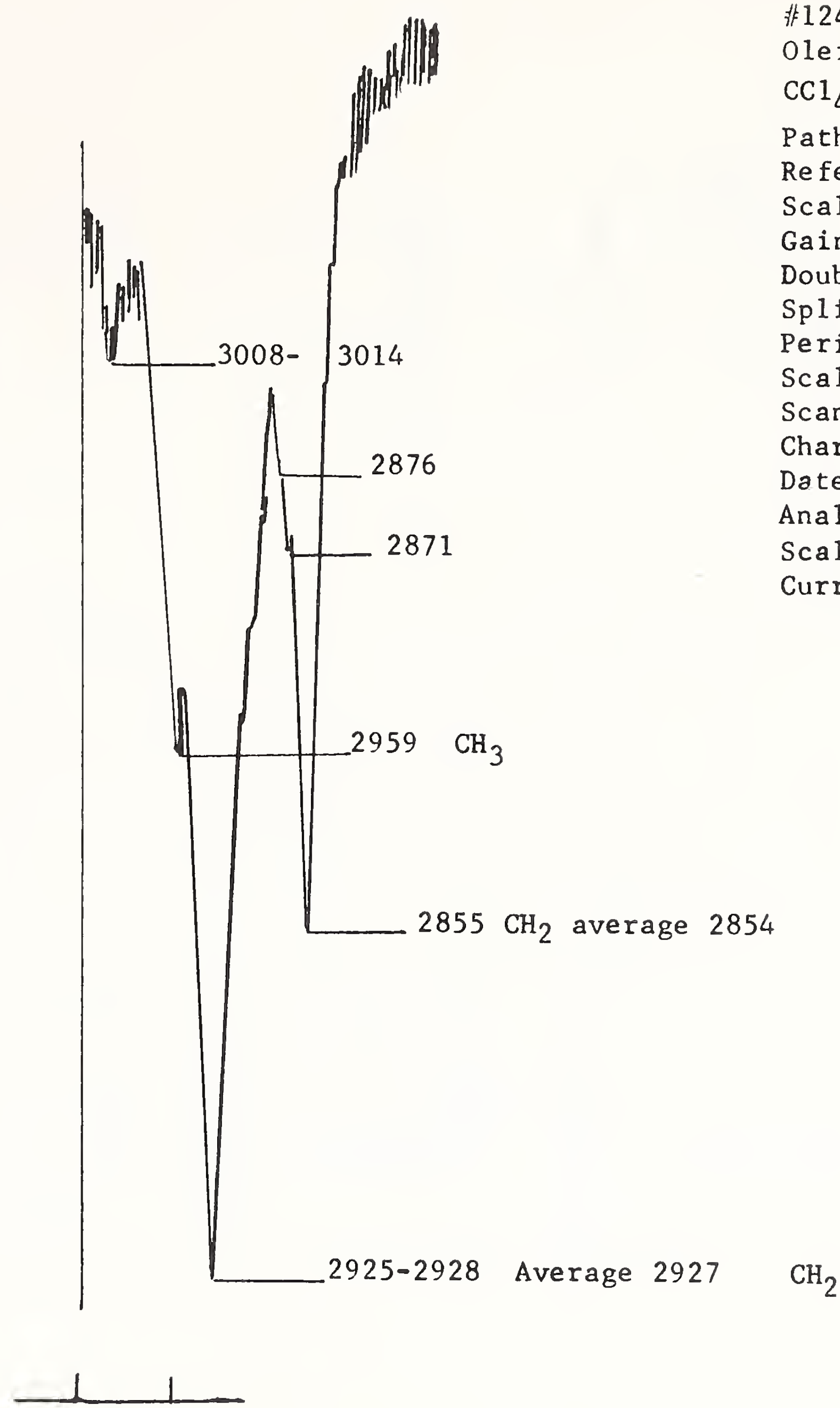
SAMPLE NAME	TYPE OF SAMPLE	NOTES	DATE SAMPLE PREPARED
Oils by fullers earth from distillation residue of Phillips MC-800	Slide	Easy to work with	9-21-64
Cyclics from petrolenes from distillation residue of Conoco MC-800	Slide	Easy to work with	9-21-64
Saturates from petrolenes from distillation residue of Conoco MC-800	Slide	Had to be heated	9-21-64
Saturates 40% Diamond 100-120 Aged 11 months in air tight can	Slide	Easy to work with	9-22-64
Cyclics 23% Diamond 100-120 Aged 11 months in air tight can	Slide	Easy to work with	9-22-64
Cyclics from petrolenes from distillation residue of Phillips MC-800	Slide	Easy to work with	9-22-64
Asphaltics from Conoco thin film blend of 97 pen	Slurry	Dried by Infra-red	10-5-64
Cyclics from Conoco thin film	2 salt plates	Had to be put between 2 salt plates because of the thinness	10-5-64
Saturates 39.34% Distillation Residue Phillips MC-800 TSSMethod	Slide		
Cyclics Distillation Res. Phillips MC-800 TSSMethod Sept. 4	Slide		
Resins Distillation Residue Phillips MC-800 16.89% Sept. 4, 64 TSSM	Slide		

SAMPLE NAME	TYPE OF SAMPLE	NOTES	DATE SAMPLE PREPARED
Asphaltenes 20.45% Distillation Residue From Phillips MC-800 TSSMethod	Slide		
Cyclics 42% Conoco 100-120 aged in air tight can 11 months	Slide	Slide, easy to work with	Run 10-1-64
Asphaltics 31% Conoco 105 pen aged in air tight can for 11 months	Slide	Easy to work with	Run 10-2-64
Cyclics 19% from Phillips 100-120 pen aged in tin can 11 months	Slide	Easy to work with	Run 9-25-64
Saturates 43% Phillips 100-120 aged in tin can for 11 months	Slide	Easy to work with	9-25-64
Saturates from petrolenes from distillation residue of Phillips MC-800	Slide	Easy to work with	9-25-64
Saturates 26% Conoco 100-120 aged in air tight can for 11 months	Slide	Easy to work with	9-28-64
Saturates 52.6% Humble 100-120 pen Aged in air tight can for 11 months	Slide	Easy to work with	9-29-64
Conoco 97 pen from thin film	Slide	Had to be heated	10-5-64
Asphaltics 25.4% Humble 100-120 Aged in air tight can at room temp. for 11 months	Slurry	CCl_4 Dried by Infra-red lamp	10-6-64
Farmers MC-800 with Darakote. Heat resistant refinery grade 1 to 100	Slide	Easy to work with	10-7-64

SAMPLE NAME	TYPE OF SAMPLE	NOTES	DATE SAMPLE PREPARED
Farmers MC-800 Plain	Slide	Easy to work with	10-7-64
Asphaltics 37% Diamond 100-120 Aged in air tight can for 11 months	Slurry	Dried with IR lamp CCl_4 added	10-9-64
Darakote Maintenance Grade	Between 2 salt plates .025 spacer	Easy to work with	10-9-64
Humble MC-800 Plain	Slide	Easy to work with	10-13-64
Conoco MC-3000 Plain	Slide	Easy to work with	10-13-64
Conoco MC-3000 with Darakote. Heat resistant refinery grade 1 to 100	Slide	Easy to work with	10-14-64
Phillips MC-800 Darakote. Heat resistant univer-sal grade 1-100	Slide	Easy to work with	10-14-64
Resins from Conoco thin film blend of 97 pen 6-3-64	Slurry	CCl_4 used and dried by IR lamp	10-14-64
Big West SC-800	Slide	Easy to work with	10-16-64
Darakote Heat resistant Universal grade	Slide	Easy to work with	10-16-64
Darakote Universal grade Heat resistant	Slide	Easy to work with	10-16-64

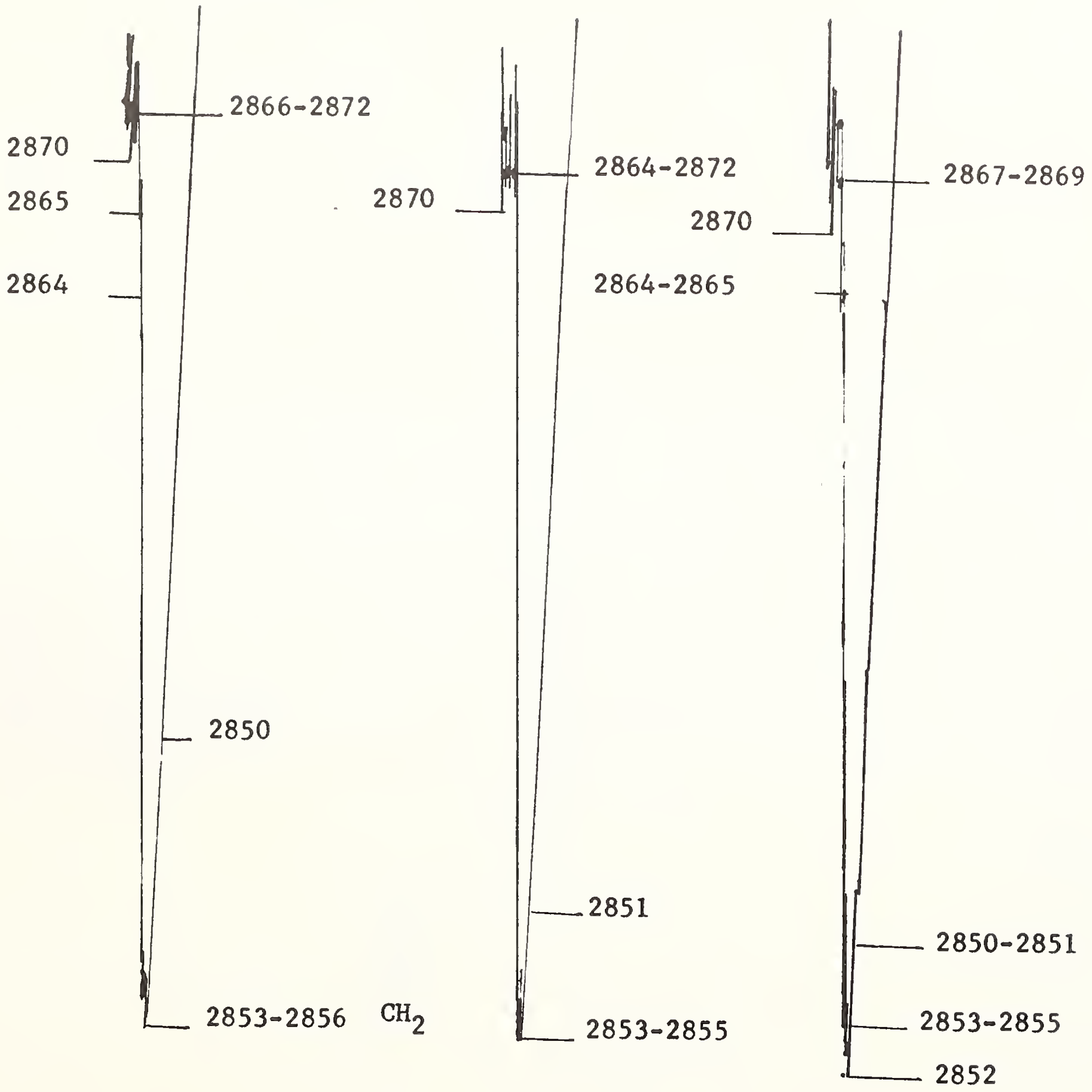
SAMPLE NAME	TYPE OF SAMPLE	NOTES	DATE SAMPLE PREPARED
Saturates Conoco 108 pen after exposure on roof for 1 yr. Pen after exposure was 38	Slide	Easy to work	11-2-64
Conoco 108 pen after 1 yr. in air tight can at room temperature	Slide	Easy to work with	11-2-64
Conoco asphalt after exposure on roof for 1 year. Pen 38	Slide	Heated on hot plate	11-4-64
Conoco Base Asphalt. Pen 0 November 4,'64	Slurry	CCl_4 dried with infra-red lamp	11-6-64
Cyclics 42.3% from Conoco 108 pen after 1 yr. in an air tight can at room temp.	Slide	Easy to work	10-29-64
Asphaltenes 32.9% From Conoco 38 pen After exposure under glass on lab roof for 1 year	Slide	Easy to work	10-30-64
Saturates 30.3% from Conoco 108 pen after 1 yr. in air tight can at room temp.	Slide	Easy to work with	10-30-64
Asphaltenes 27.8% Oct. 20,'64 From Conoco 108 pen after 1 yr. in air tight can at room temp. Asphaltenes by n-pentane	Slurry	Dried by an infra-red lamp	11-2-64


Beckman
WAVELENGTH IN MICRONS
FREQUENCY IN CM⁻¹
C=O STRETCH
O-H STRETCH
OH
CH₂
CH₂
CH₃



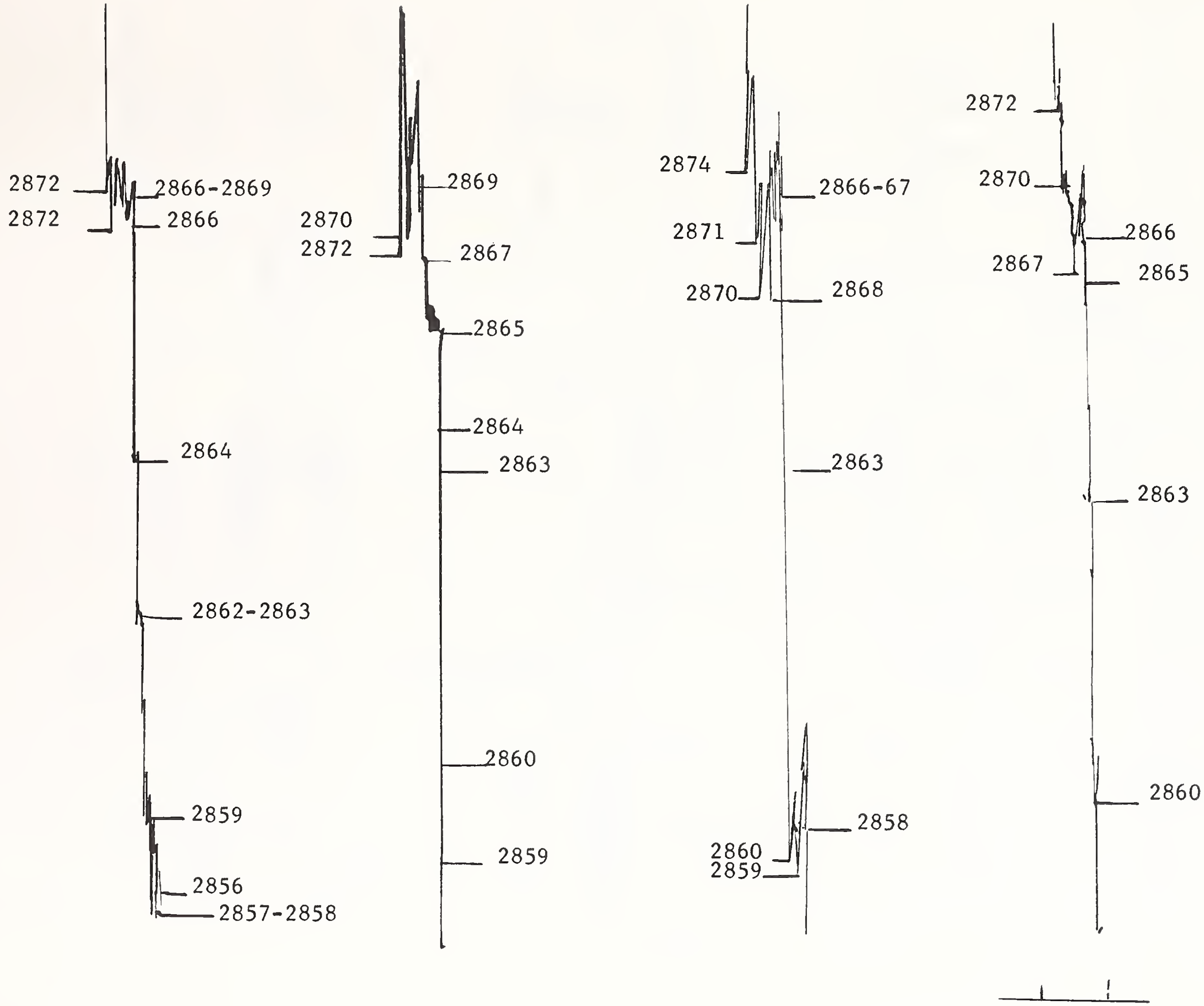
#12464 Oleic 2
Oleic Acid (1:1000
CCl_4 (

Path 0.406 mm
Reference Air
Scale Selection 0-100%
Gain 100 x .206
Double Beam
Split X
Period 8
Scale Expansion 20-80 full
Scanning Speed $8 cm^{-1}/min.$
Chart Speed $100 cm^{-1}/in.$
Date 1-27-64
Analyst - Lee
Scale Contract Off
Current .6

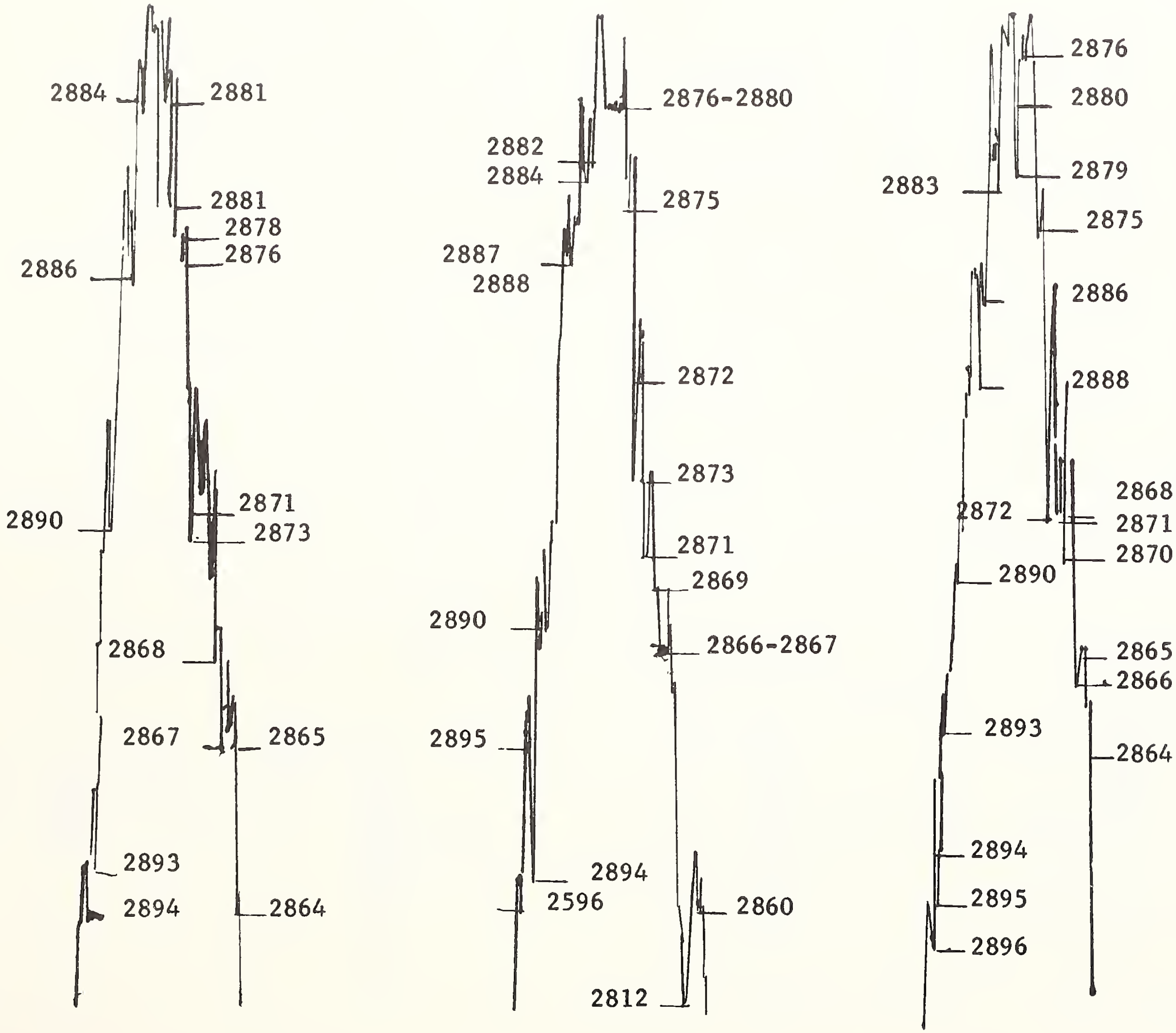


#12464 Oleic 3
Oleic Acid (1:1000
CCl_4 (
Path 0.406 mm
Reference Air
Scale Selection 0-100%
Gain 100 x .206
Double Beam
Slit X
Period 32
Scale Contract Off
Current .6
Scale Expansion 19-25 full
Scanning Speed $8cm^{-1}$/min.
Chart Speed $50cm^{-1}$/in.
Date 1-27-64
Analyst - Lee

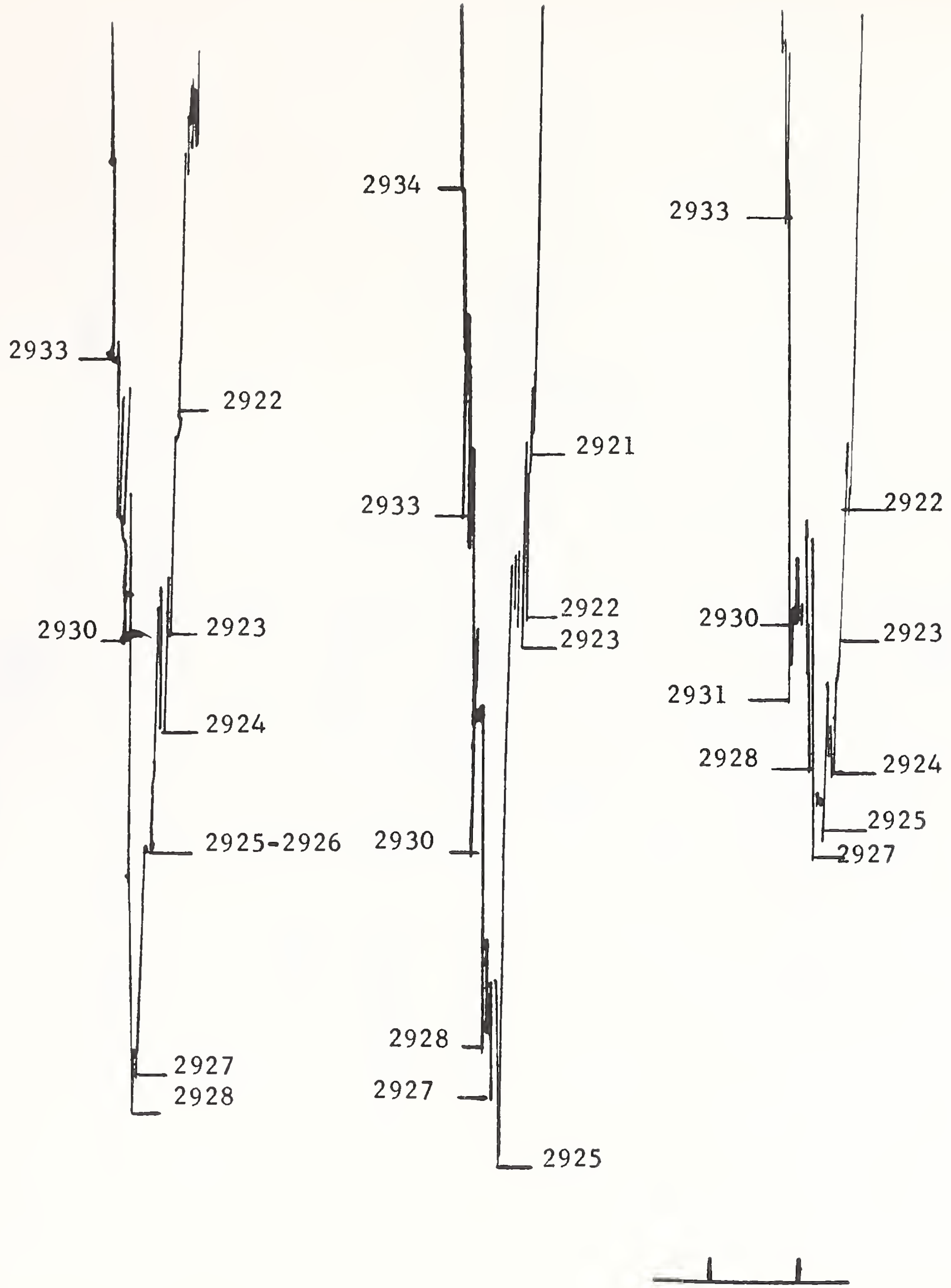
	CH_2
Average	2854



#12464 Oleic 4
Oleic Acid(1:1000
CCl_4 (
Path 0.406 mm
Reference Air
Scale Selection 0-100%
Gain 100 x .206
Double Beam
Slit x
Period 32
Scale Contract Off
Current .6
Scale Expansion 20-34 full
Scanning Speed 1.6cm^{-1}/min.
Chart Speed 20cm^{-1}/in.
Date 1-27-64
Analyst - Lee

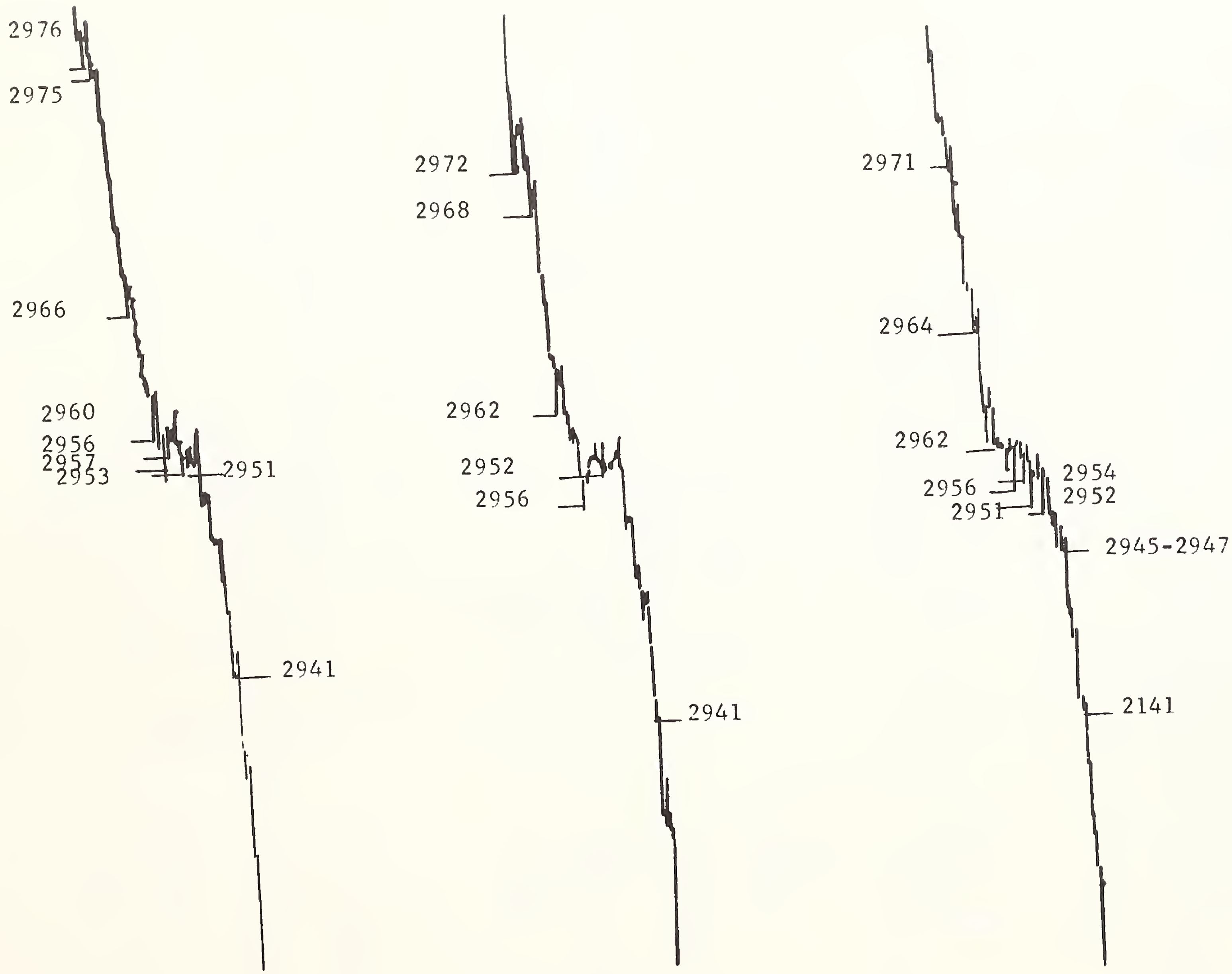


#12464 Oleic 5
Oleic Acid(1:1000
CCl_4 (
Path 0.406 mm
Reference Air
Scale Selection 0-100%
Gain 100 x .206
Double Beam
Slit X
Period 32
Scale Contract Off
Current .6
Scale Expansion 22-26 full
Scanning Speed 1.6cm^{-1}/min.
Chart Speed 20cm^{-1}/in.
Date 1-27-64
Analyst - Lee

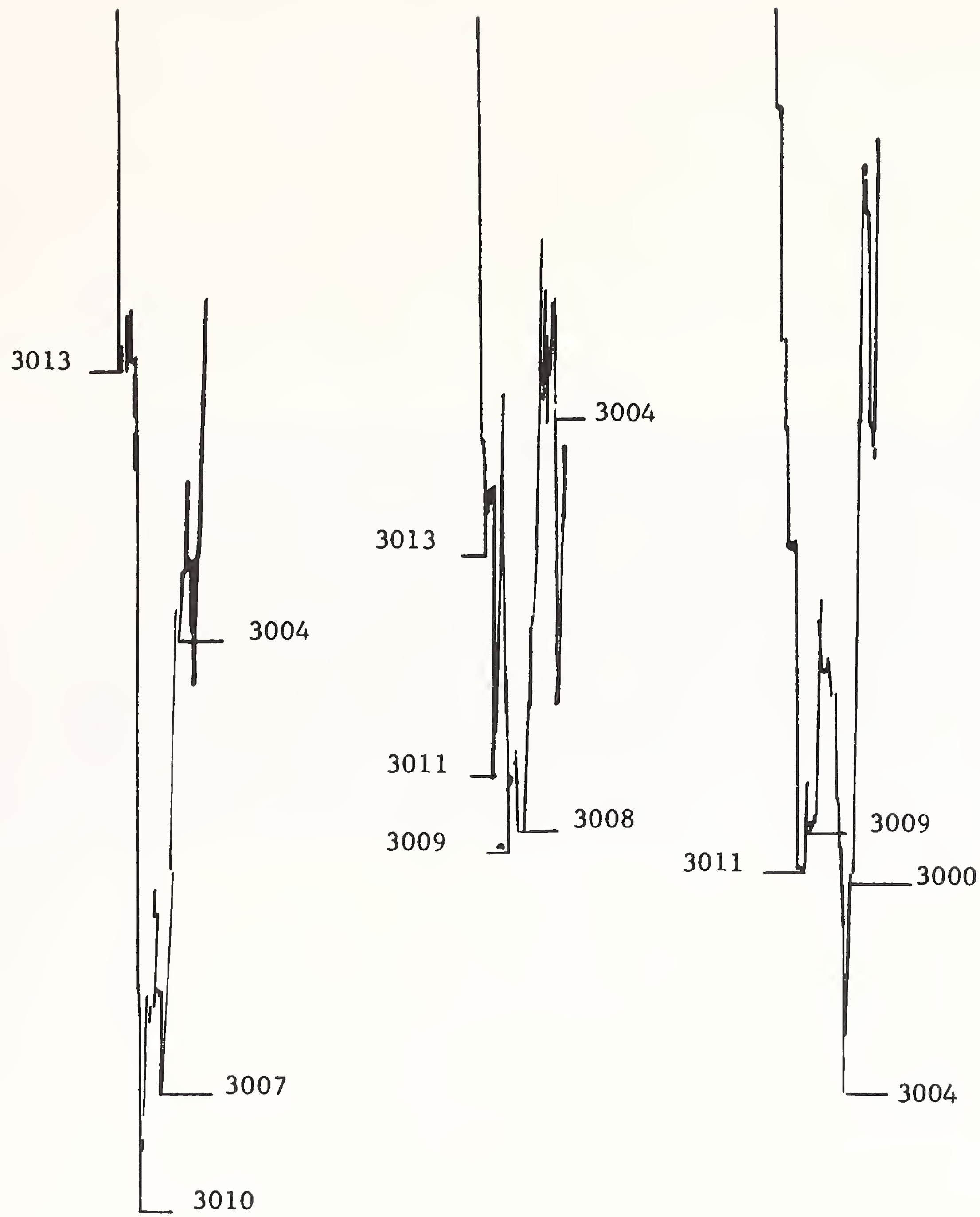


#12464 Oleic 6
Oleic Acid (1:1000
CCl_4 (
Path 0.406 mm
Reference Air
Scale Selection 0-100%
Gain 100 x .206
Double Beam
Slit X
Period 32
Scale Contract Off
Current .6
Scale expansion 14-18 full
Scanning Speed 1.6cm^{-1}/min.
Chart Speed 20cm^{-1}/in.
Date 1-27-64
Analyst - Lee

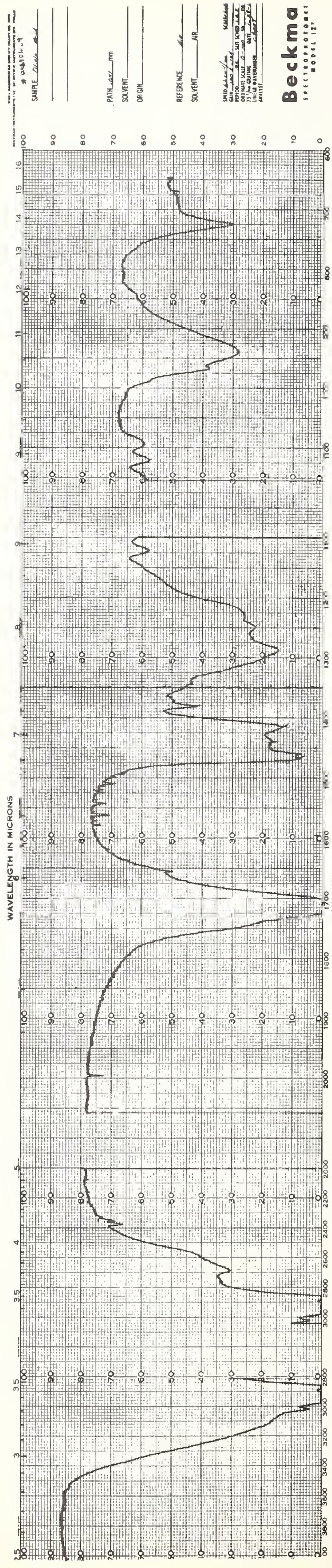
Average 2927



#12464 Oleic 7
Oleic Acid ($1:1000$
CCl_4 (
Path 0.406 mm
Reference Air
Scale Selection 0-100%
Gain 100 x .206
Double Beam
Slit X
Period 32
Scale Contract Off
Current .6
Scale Expansion 26.30 full
Scanning Speed 1.6cm^{-1}/min
Chart Speed 20 cm^{-1}/in.
Date 1-27-64
Analyst - Lee

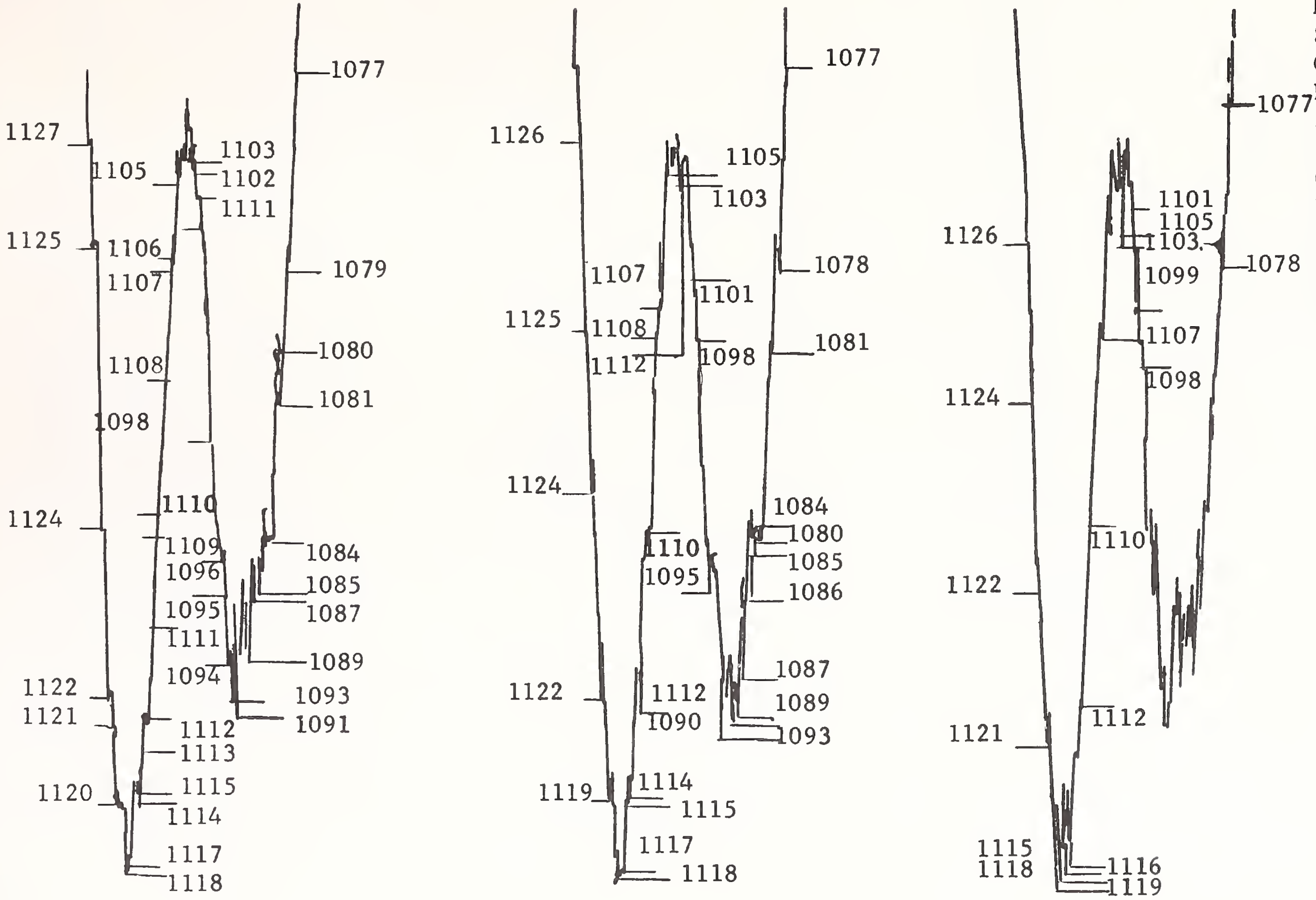


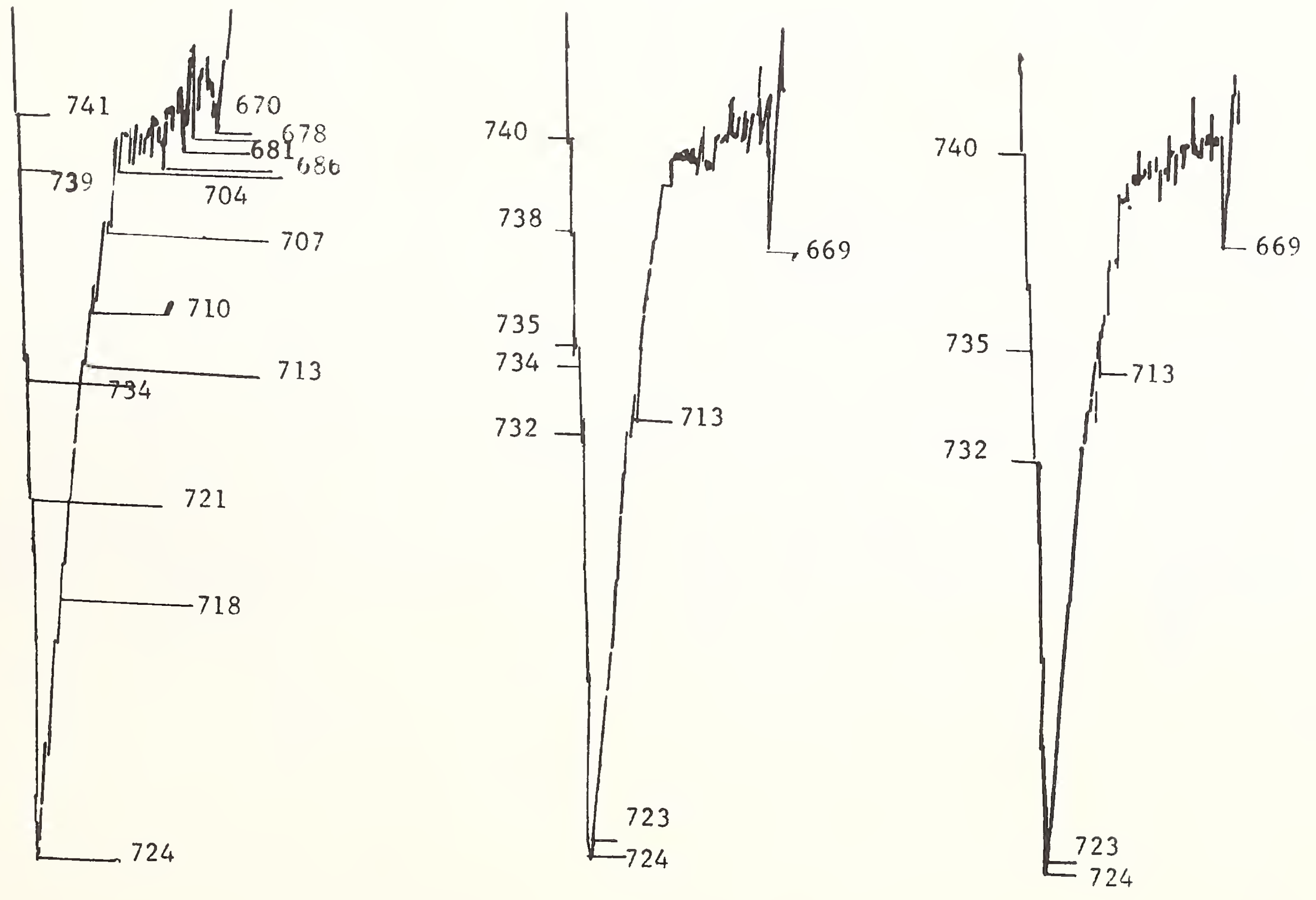
#12464 Oleic 8
Oleic Acid (1:1000
CCl_4 (
Path 0.406 mm
Reference Air
Scale Selection 0-100%
Gain 100 x .206
Double Beam
Slit X
Period 8
Scale Contract Off
Current .6
Scale Expansion 76-80 full
Scanning Speed 8 cm^{-1}/min.
Chart Speed 100 cm^{-1}/in.
Date 1-27-64
Analyst - Lee



WAVELENGTH IN MICRONS
FREQUENCY IN CM⁻¹
Beckman
SPECTROPHOTOMETER

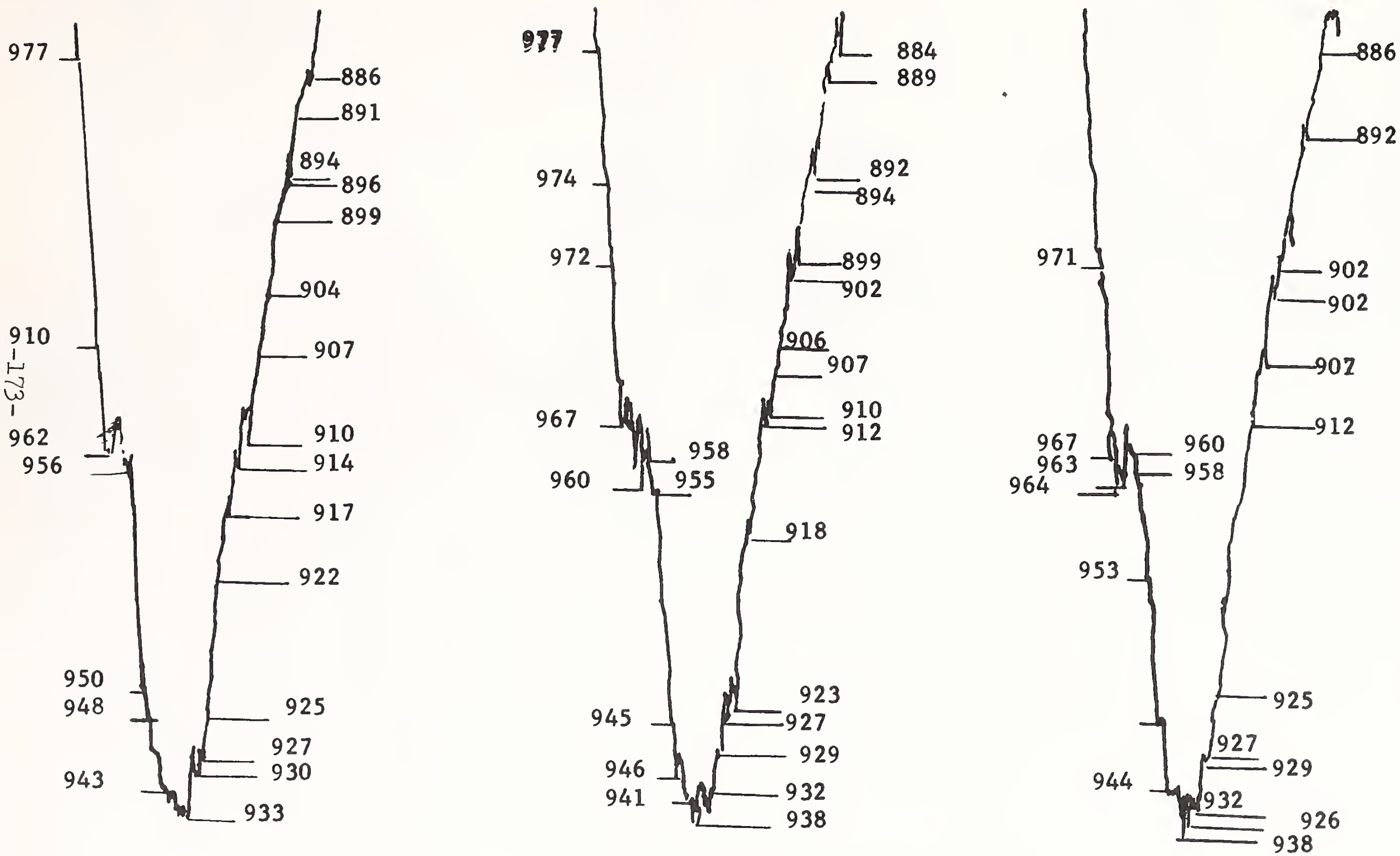
#12464 Oleic 10
Oleic Acid
Path 0.203
Reference Air
Scale Selection 0-100
Gain Selling 100 x 124
Double Beam
Split 1.2 x
Scanning Speed 1.6 cm^{-1}/min.
Chart Speed 20 cm^{-1}/in.
Period 32
Scale Expansion 10-4 full
Current .6
Date 1-28-64
Analyst - Lee

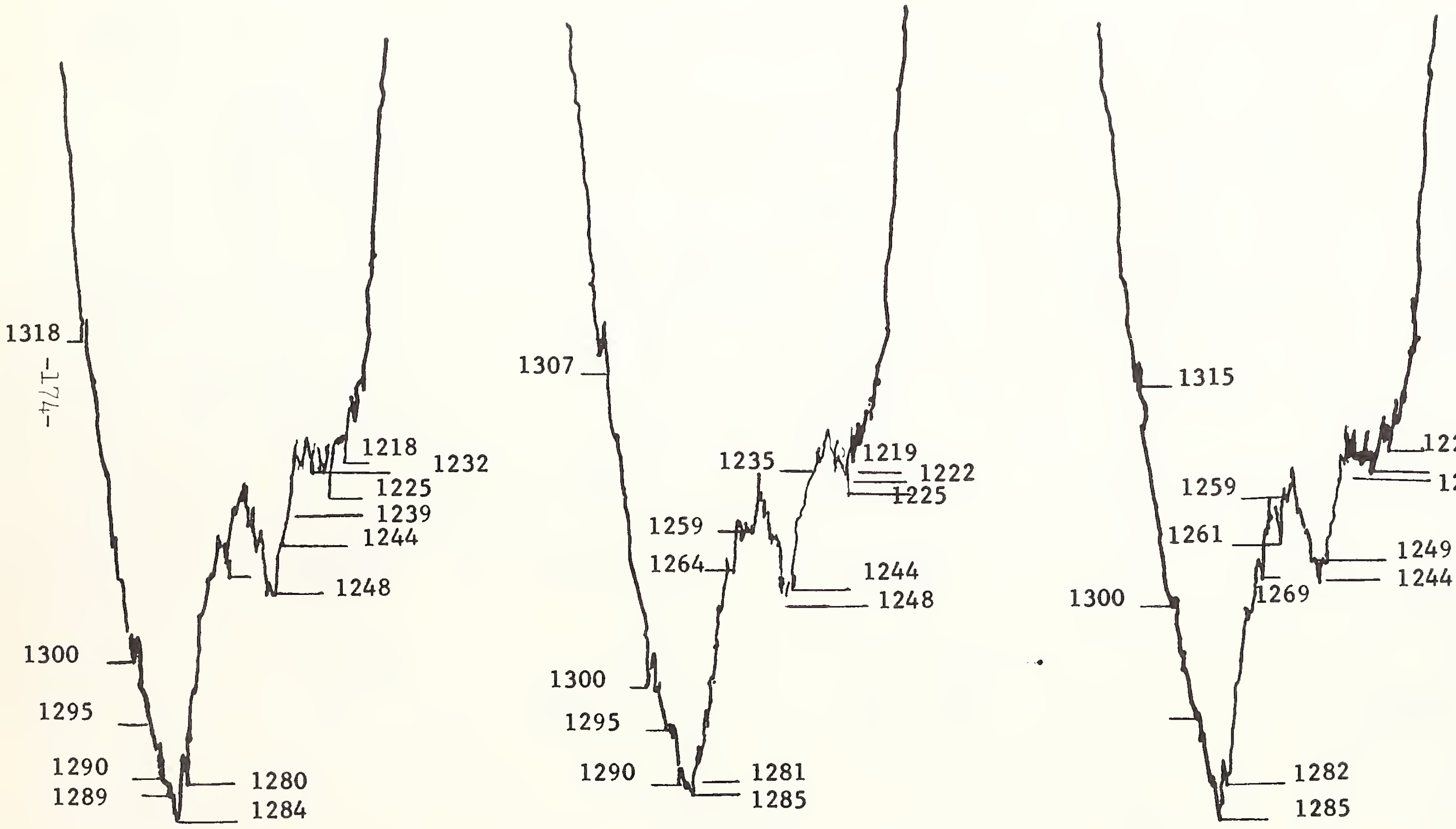




#12464 Oleic 11
Path .051
Reference Air
Scale Selection 0-100
Gain 100 x 124
Double Beam
Slit 1.2 x
Scanning Speed 3.2 cm^{-1}/min.
Chart Speed 31.25 cm^{-1}/in.
Scale Expansion 15-35 full
Period 32
Current .6
Date 1-28-64
Analyst - Lee

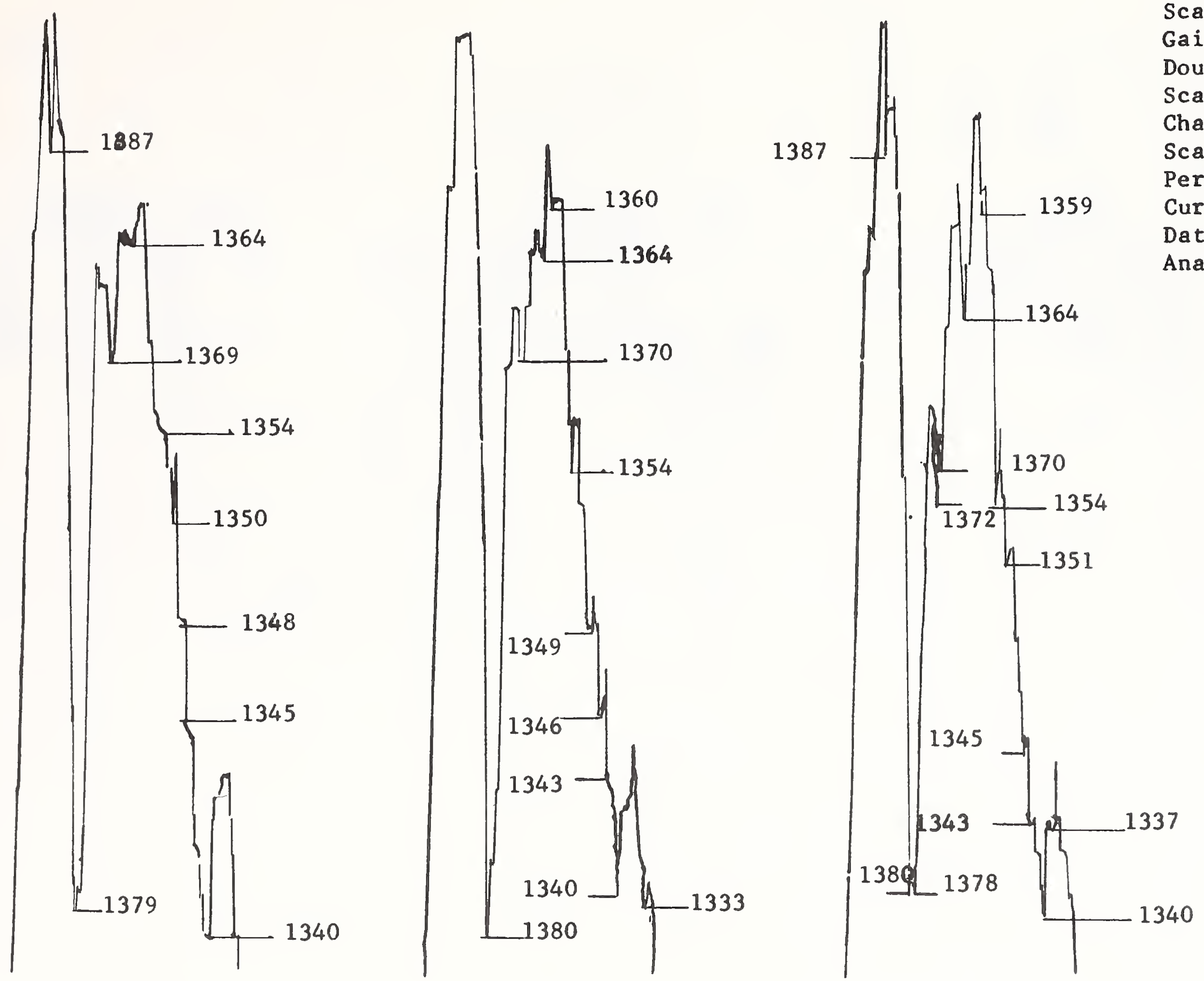
#12464 Oleic 12
Oleic Acid
Path .051
Scale Selection 0-100
Gain 100 x 1.24
Double Beam
Slit 1.2 x
Scanning Speed 5.2 cm^{-1}/min
Chart Speed 31.25 cm^{-1}/in.
Scale Expansion 10-30 full
Period 32
Current .6
Date 1-28-64
Analyst - Lee



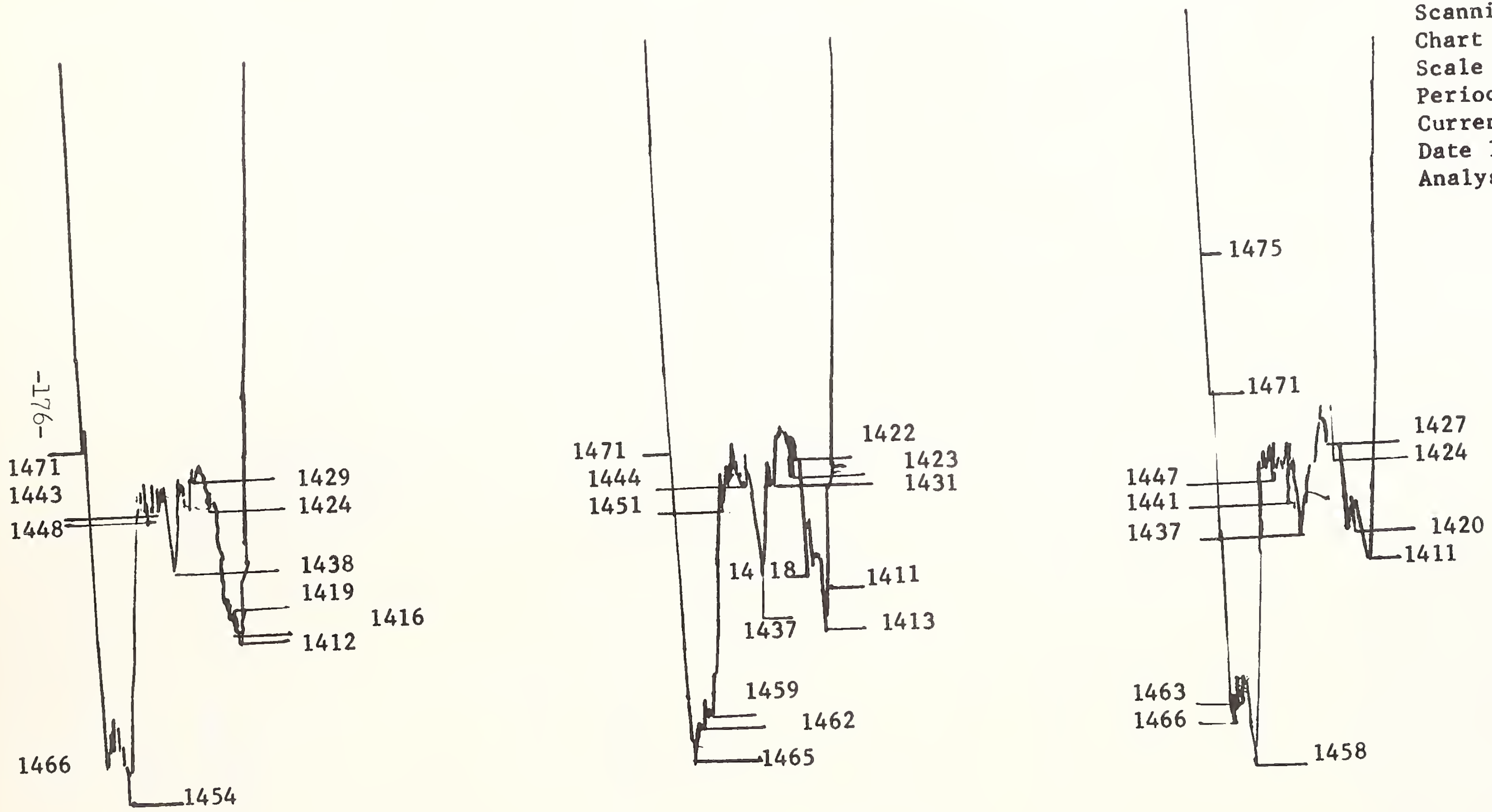


#12464 Oleic 13
Oleic Acid
Path .051
Reference Air
Scale Selection 0-100
Gain 100 x 1.24
Double Beam
Scanning Speed 3.2 cm^{-1}/mir
Chart Speed 31.25 cm^{-1}/in.
Scale Expansion 5-25 full
Period 32
Current .6
Date 1-29-64
Analyst - Lee

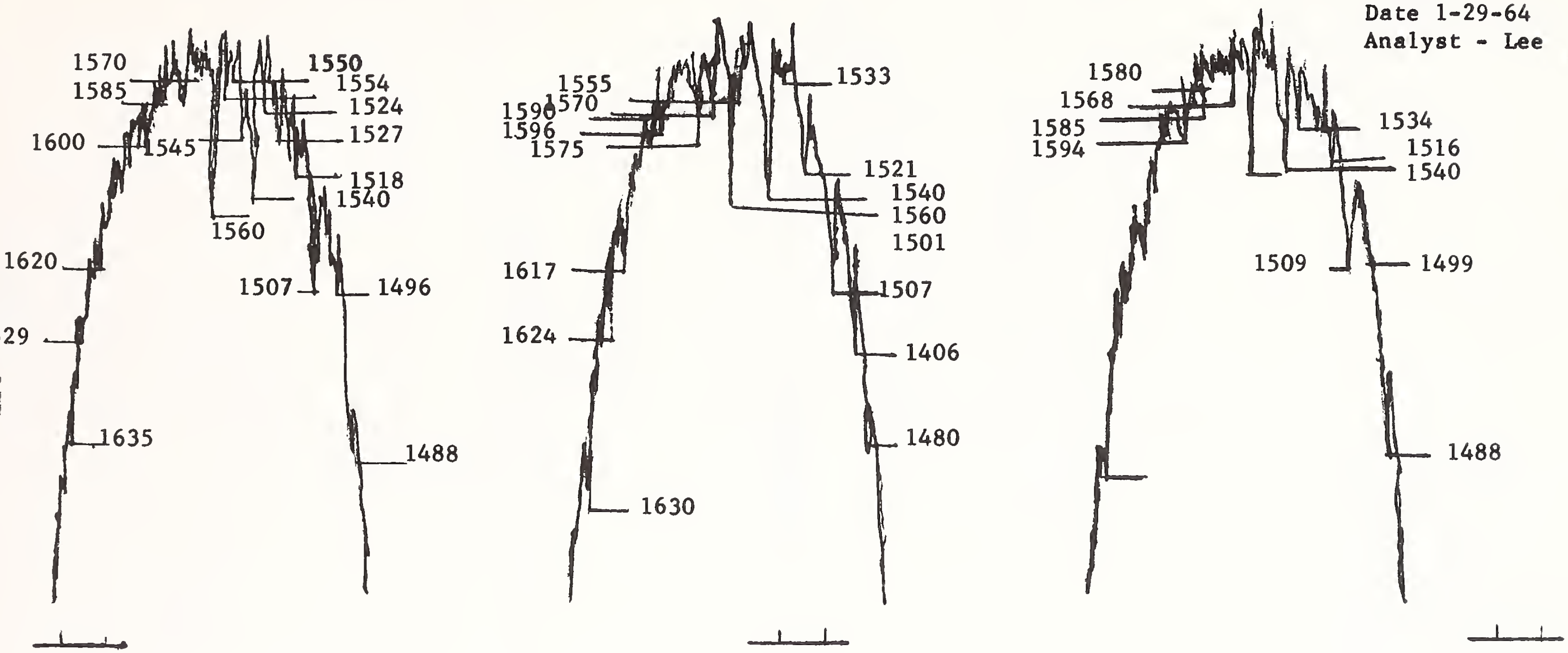
#12464 Oleic 14
Oleic Acid
Path .051
Reference Air
Scale Selection 0-100
Gain 100 x 1.24
Double Beam
Scanning Speed 8 cm^{-1}/min.
Chart Speed 31.25 cm^{-1}/in.
Scale Expansion 5-25 full
Period 32
Current .6
Date 1-29-64
Analyst - Lee

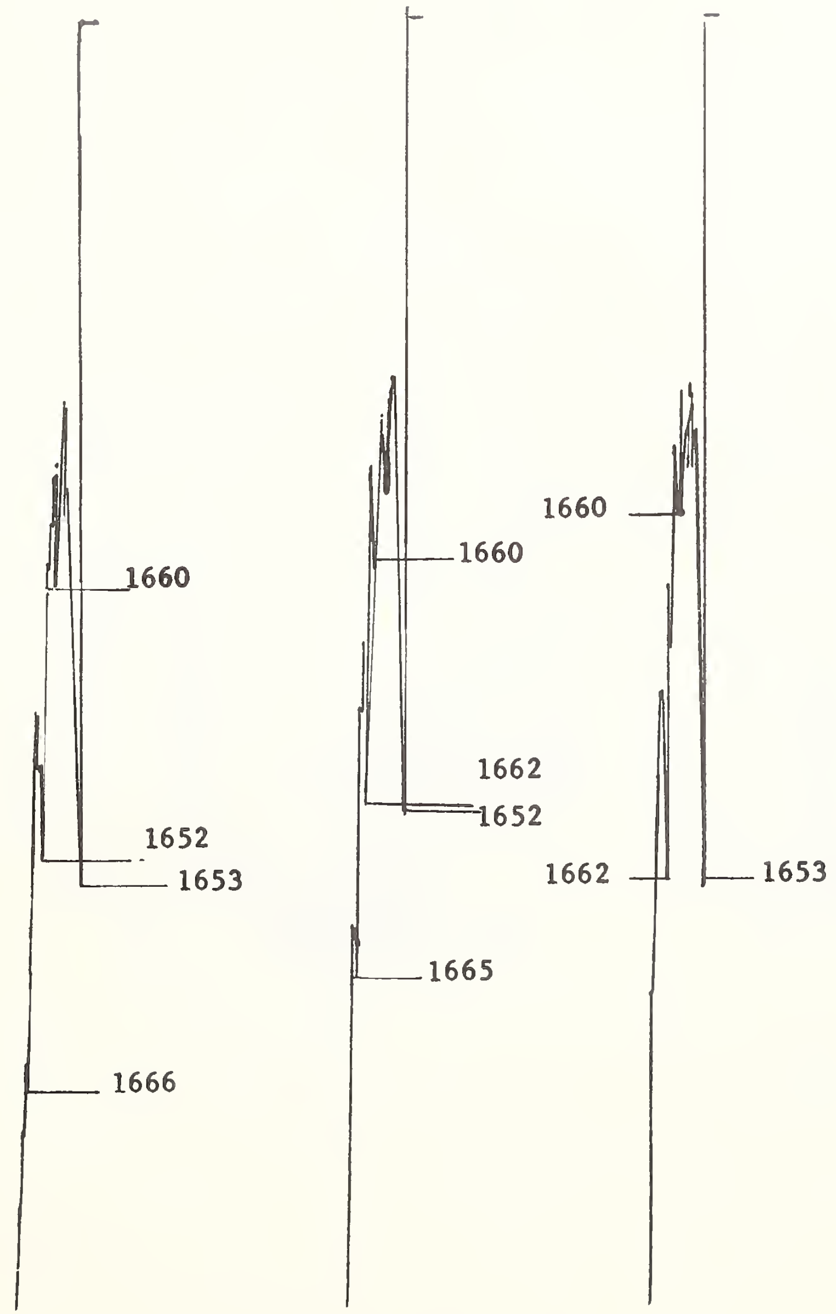


#12464 Oleic 15
Oleic Acid
Path .051
Reference Air
Scale Selection 0-100
Gain 100 x 1.24
Double Beam
Scanning Speed 8 cm^{-1}/min.
Chart Speed 31.25 cm^{-1}/in.
Scale Expansion 40-55 full
Period 32
Current .6
Date 1-29-64
Analyst - Lee

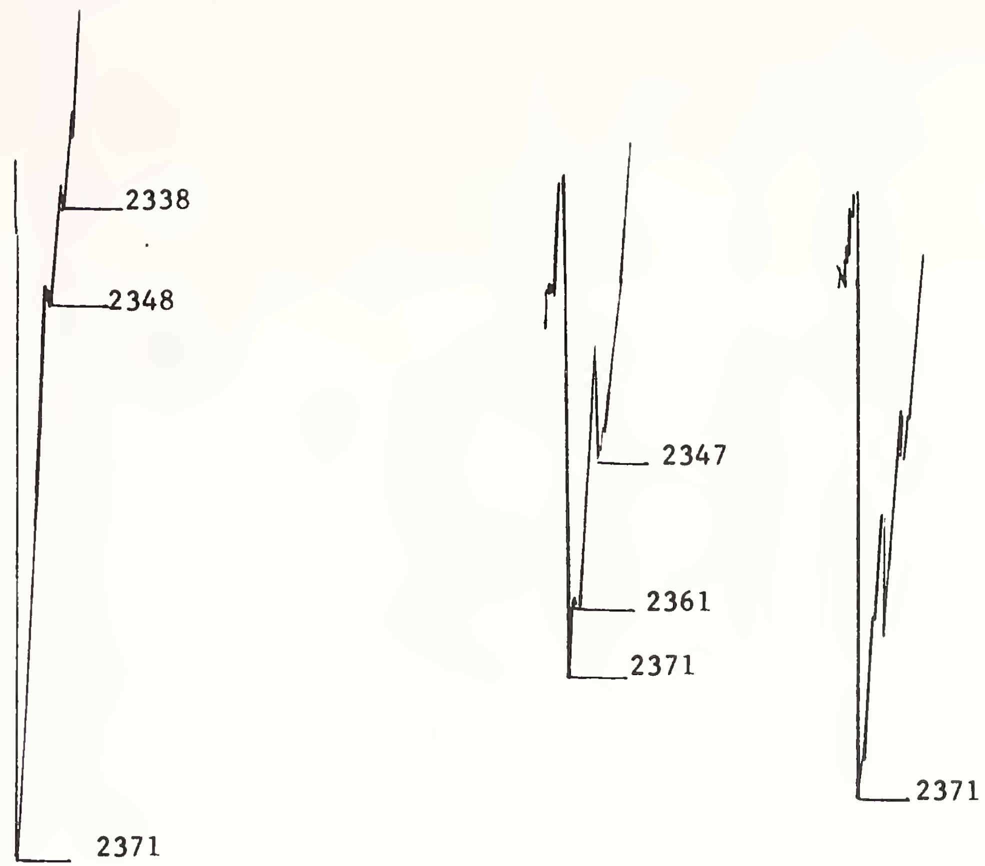


#12464 Oleic 16
Oleic Acid
Path .051
Reference Air
Scale Selection 0-100
Gain 100 x 1.24
Double Beam
Scanning Speed 20 cm^{-1}/min
Chart Speed 31.25 cm^{-1}/in.
Scale Expansion 60-80 full
Period 8
Current .6
Date 1-29-64
Analyst - Lee

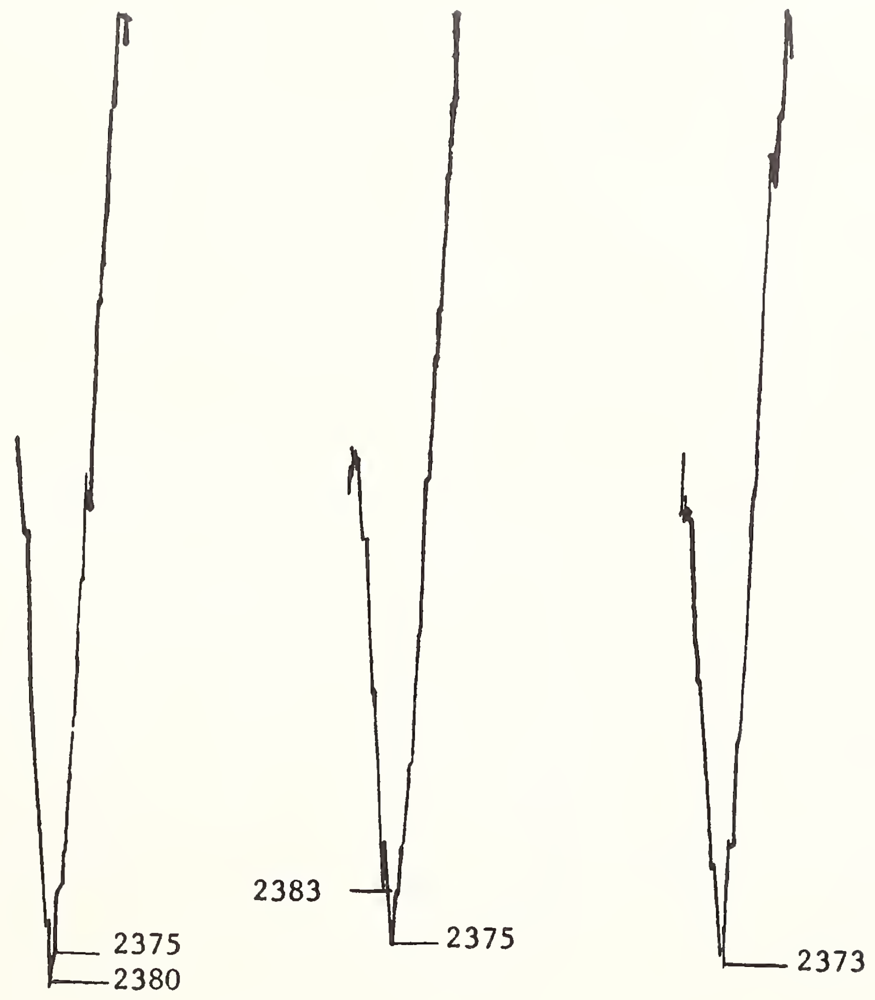




#12464 Oleic 17
Oleic Acid
Path .051
Reference Air
Scale Selection 0-100
Gain 100 x 1.24
Double Beam
Scanning Speed 1.6 cm^{-1}/min.
Chart Speed 31.25 cm^{-1}/in.
Scale Expansion 65-70 full
Period 32
Current .6
Date 1-27-64
Analyst - Lee

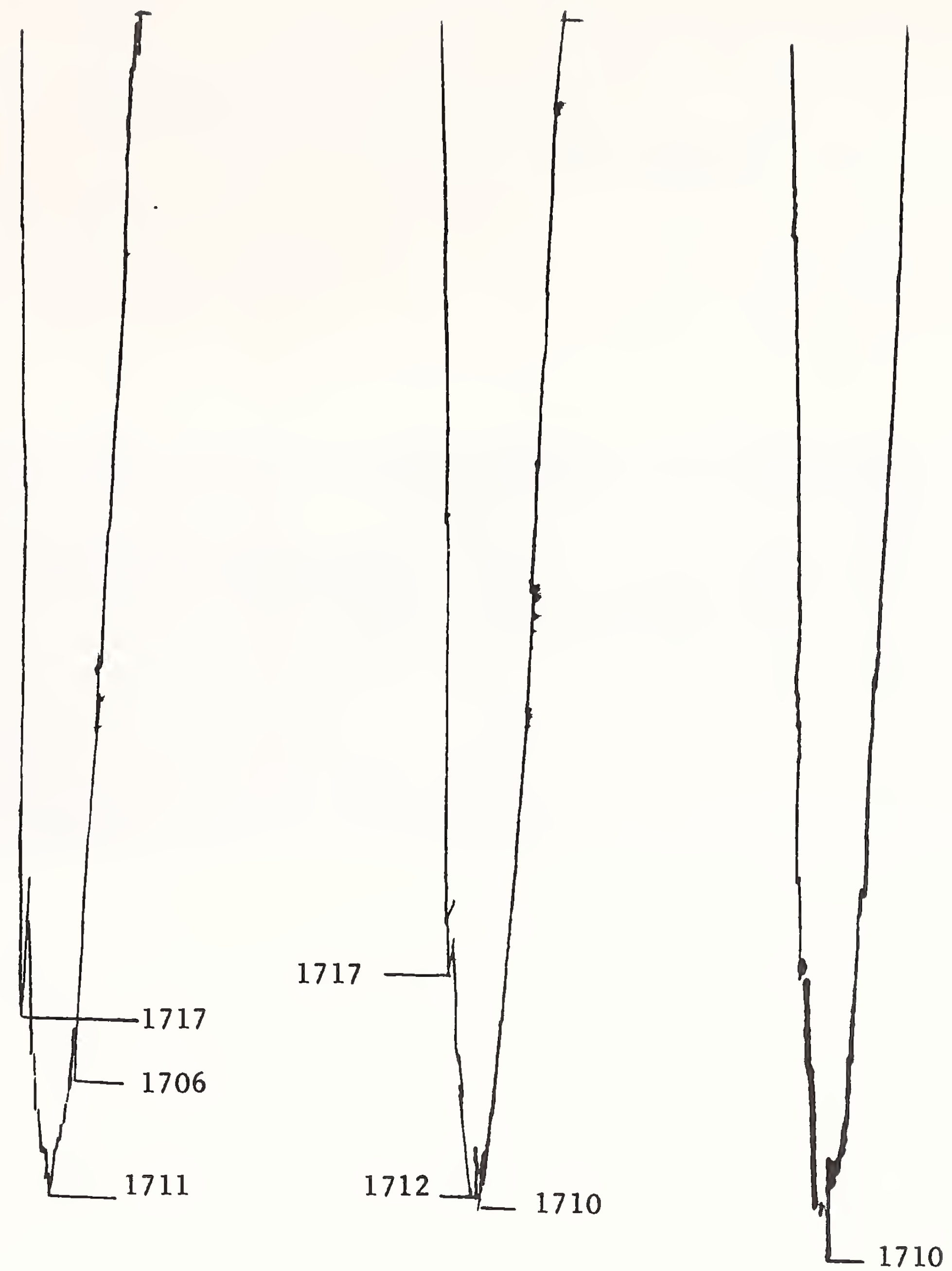


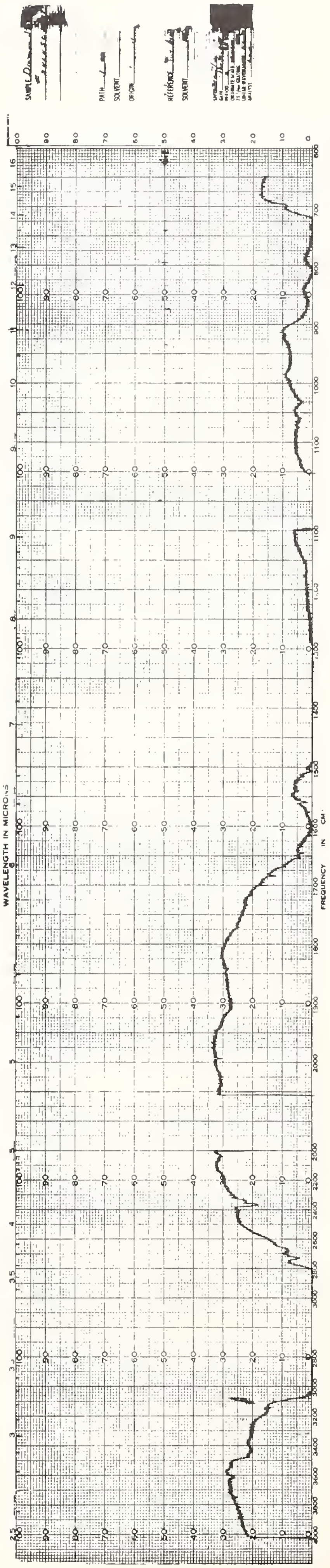
#12464 Oleic 18
Oleic Acid
Path .051
Reference Air
Scale Selection 0-100
Gain 100 x 1.24
Scanning Speed 3.2 cm^{-1}/min.
Chart Speed 125 cm^{-1}/min.
Scale Expansion 70-80 full
Period 32
Current .6
Date 1-24-64
Analyst - Lee

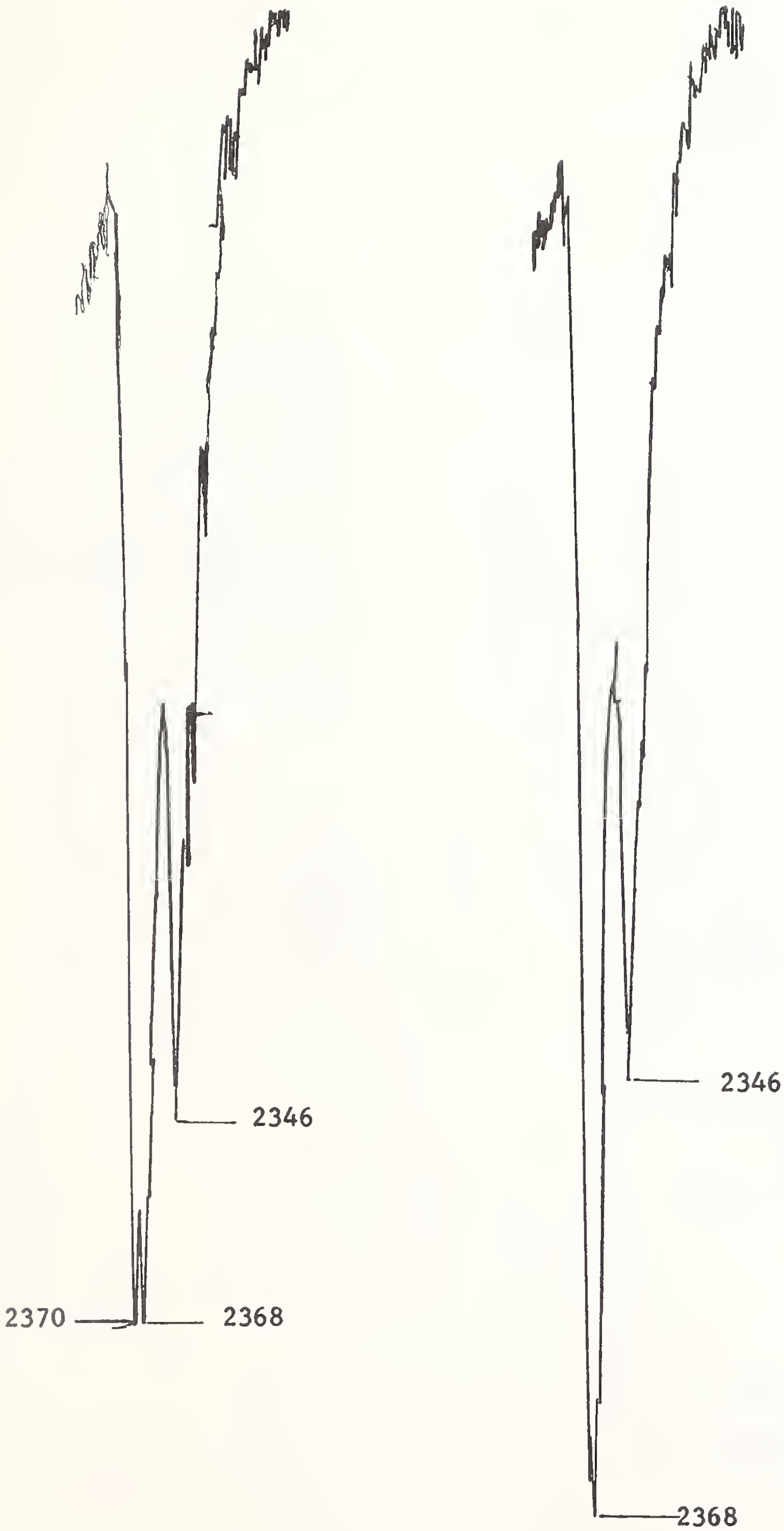


#12464 Oleic 19
Oleic Acid
Path .051
Reference Air
Scale Selection 0-100
Gain 100 x 1.24
Scanning Speed 3.2 cm^{-1}/min.
Chart Speed 1.25 cm^{-1}/in.
Scale Expansion 35-45 full
Period 32
Current .6
Date 1-29-64
Analyst - Lee

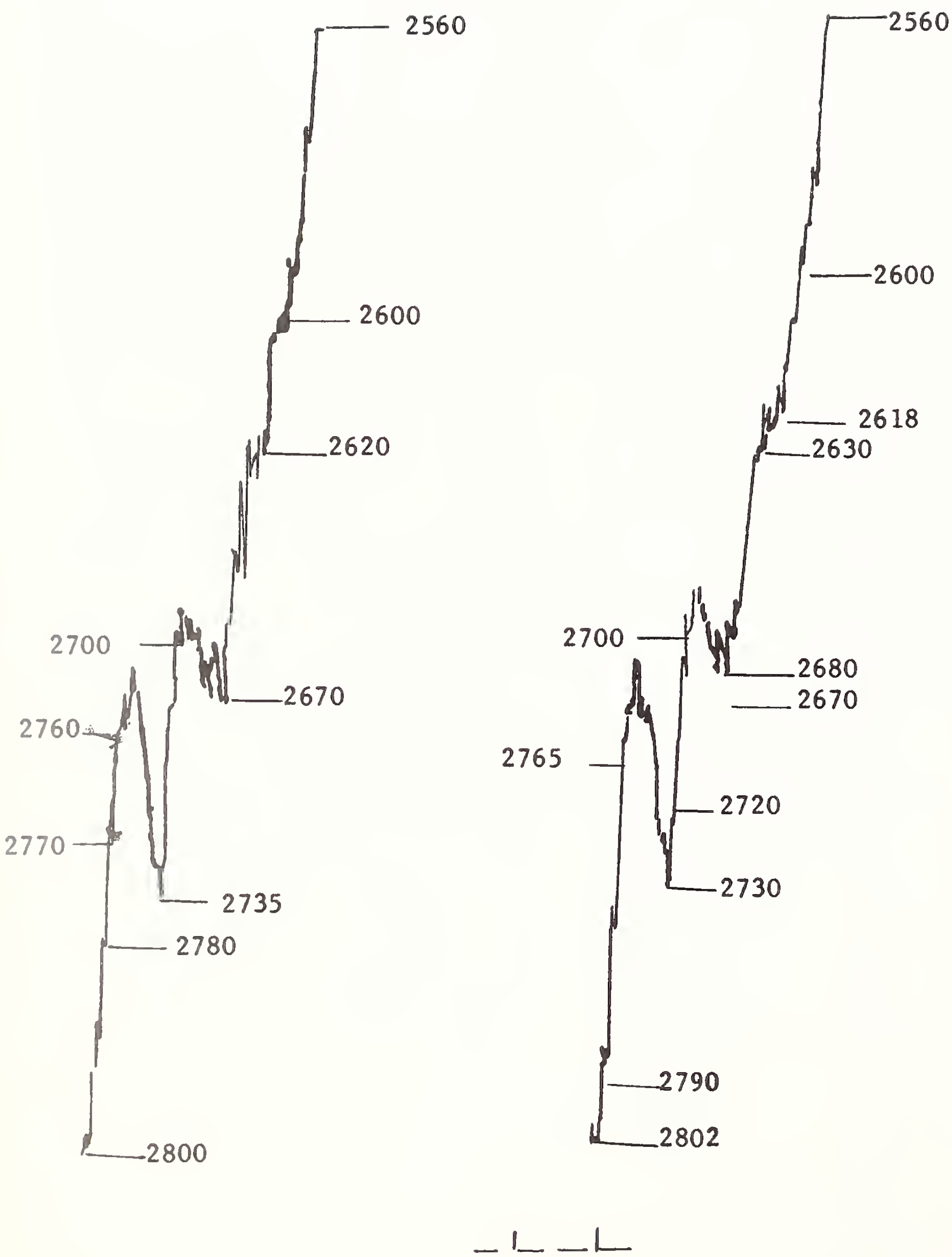
#12464 Oleic 20
Oleic Acid
Path .051
Reference Air
Scale Selection 0-100
Gain 100 x 1.24
Scanning Speed 8 cm^{-1}/min.
Chart Speed 100 cm^{-1}/min.
Scale Expansion 35-45 full
Period 8
Current .6
Date 1-29-64
Analyst - Lee



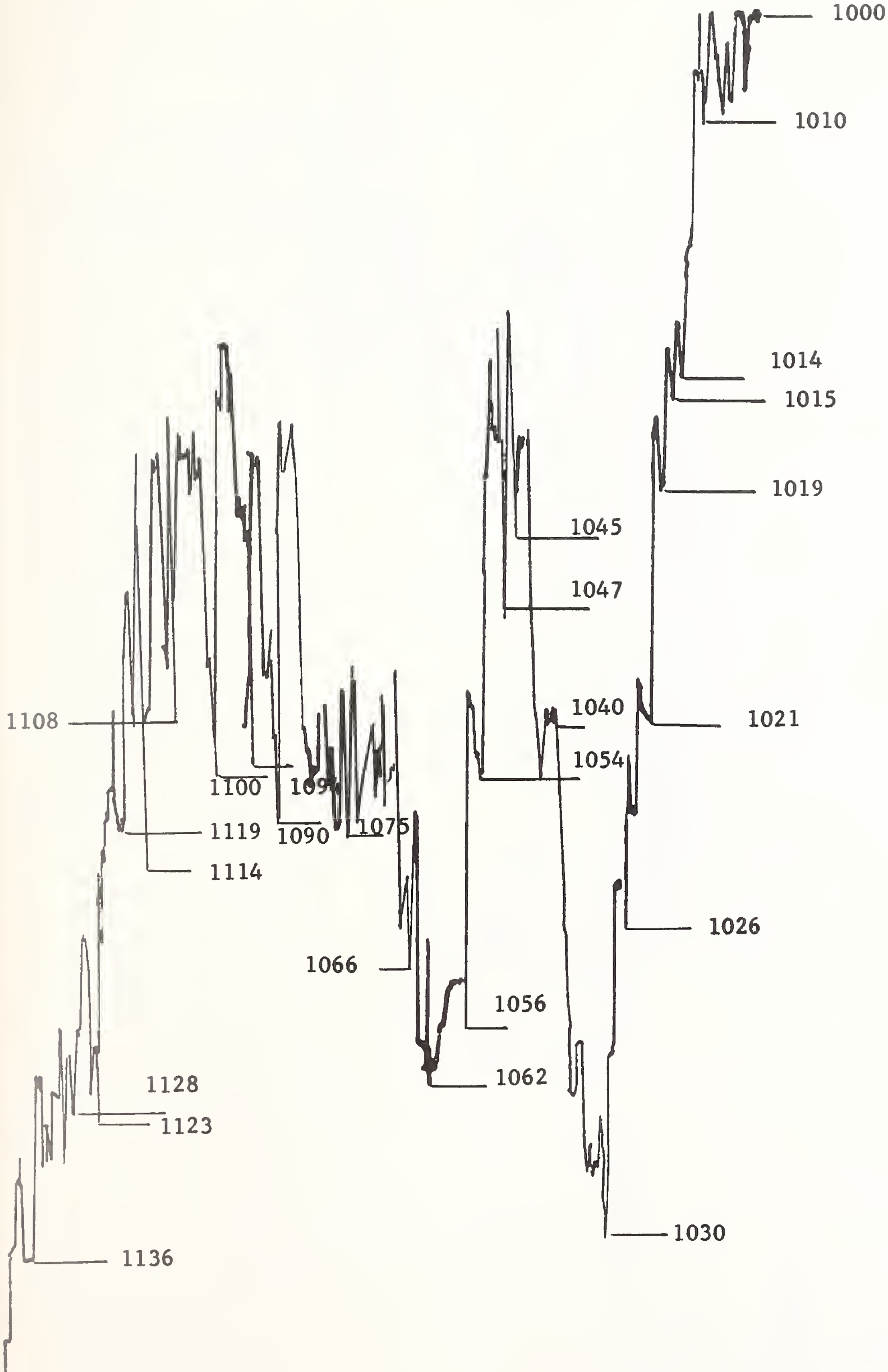

WAVELENGTH IN MICRONS
FREQUENCY IN CM



#2464 SC 2502
Diamond SC 250
Path .1 mm
Reference Air
Scale Selection 0-100
Gain 100 x .046
Scanning Speed 3.2 cm^{-1}/min.
Chart Speed 100 cm^{-1}/in.
Scale Expansion 15-30 full
Period 8
Current .6
Date 2-10-64
Analyst - Lee

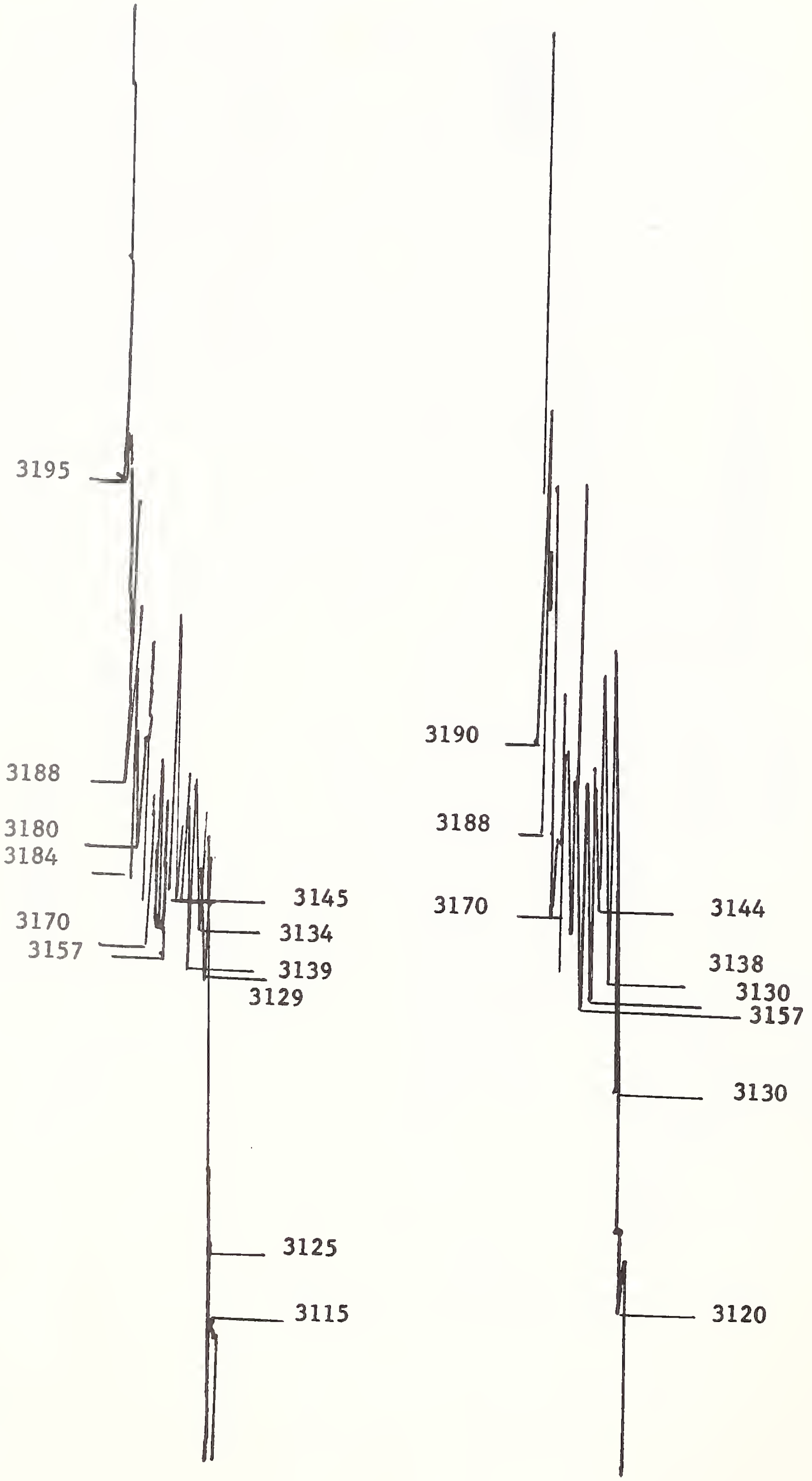


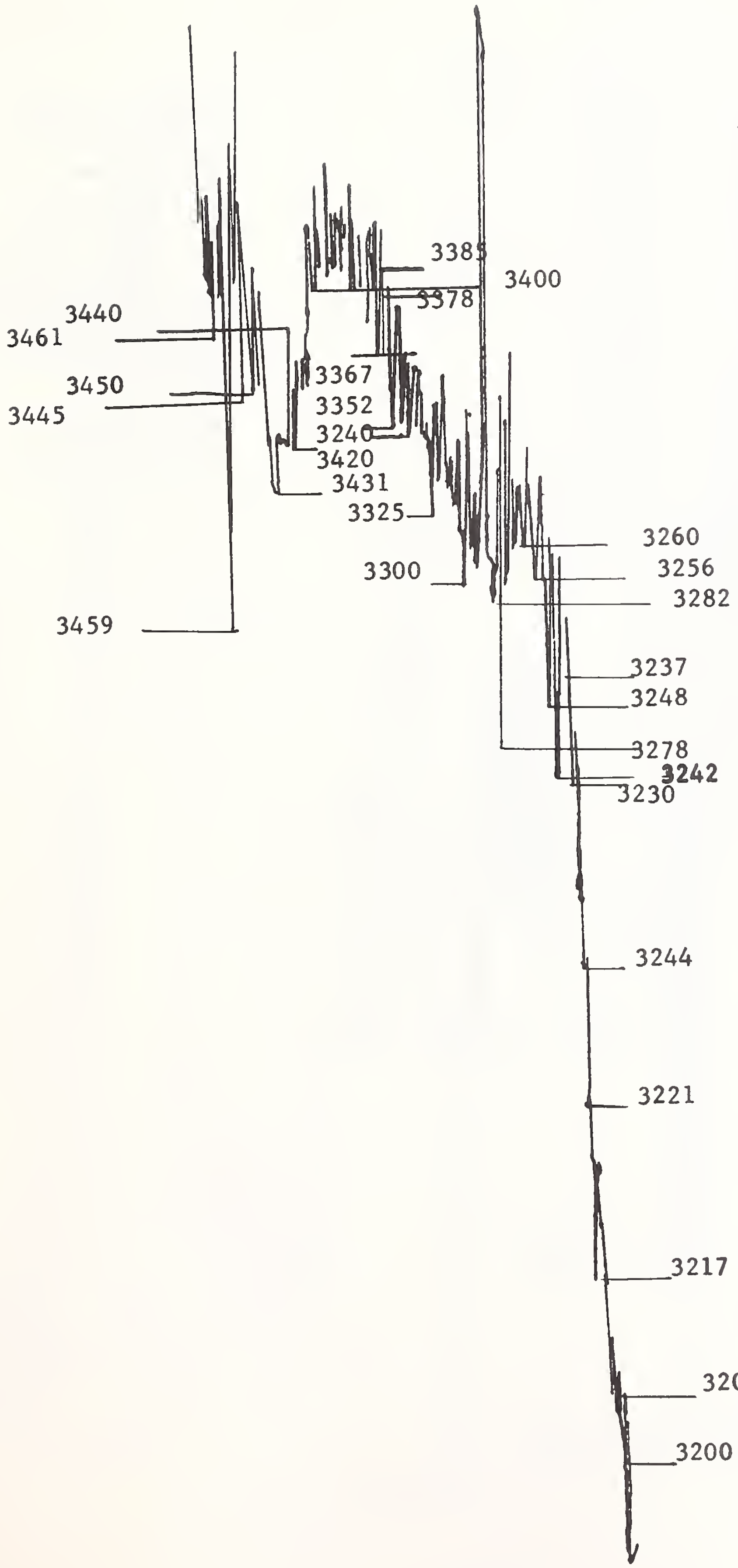
#2464 SC 2503
Diamond SC 250
Path .1 mm
Reference Air
Scale Selection 0-100
Gain 100 x .046
Scanning Speed 8 cm^{-1}/min.
Chart Speed 100 cm^{-1}/in.
Scale Expansion 0-100 full
Period 8
Current .6
Date 2-10-64
Analyst - Lee



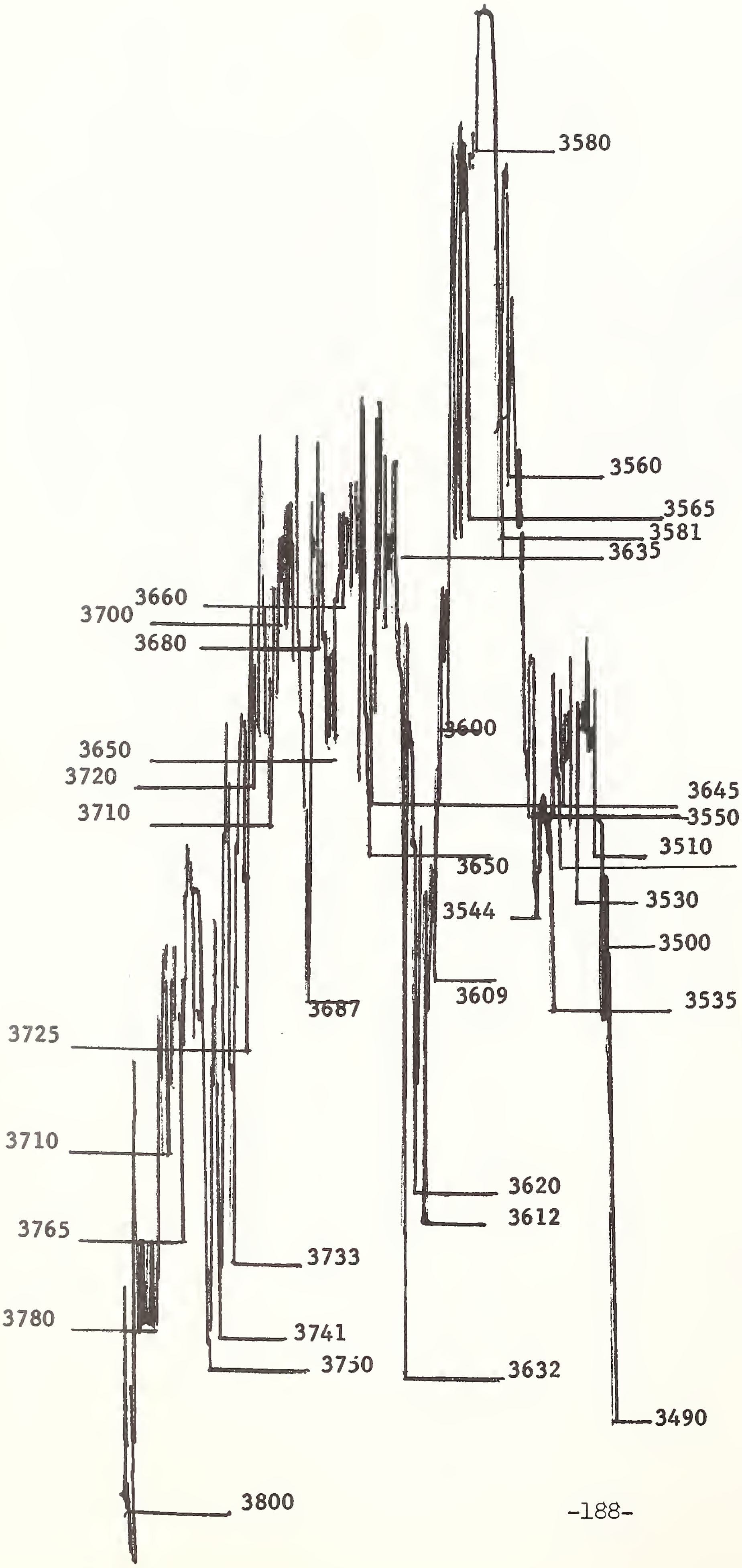
#2464 SC 2504
Diamond SC 250
Path .1 mm
Reference Air
Scale Selection 0-100
Gain 100 x .046
Scanning Speed 8 cm^{-1}/min.
Chart Speed 25 cm^{-1}/in.
Scale Expansion 2-8 full
Period 8
Current .6
Date 2-10-64
Analyst - Lee

#2464 SC 2505
Diamond SC 250
Path .1 mm
Reference Air
Scale Selection 0-100
Gain 100 X .046
Scanning Speed 3.2 cm^{-1}/min.
Chart Speed 100 cm^{-1}/in.
Scale Expansion 13-17 full
Period 8
Current .6
Date 2-10-64
Analyst - Lee

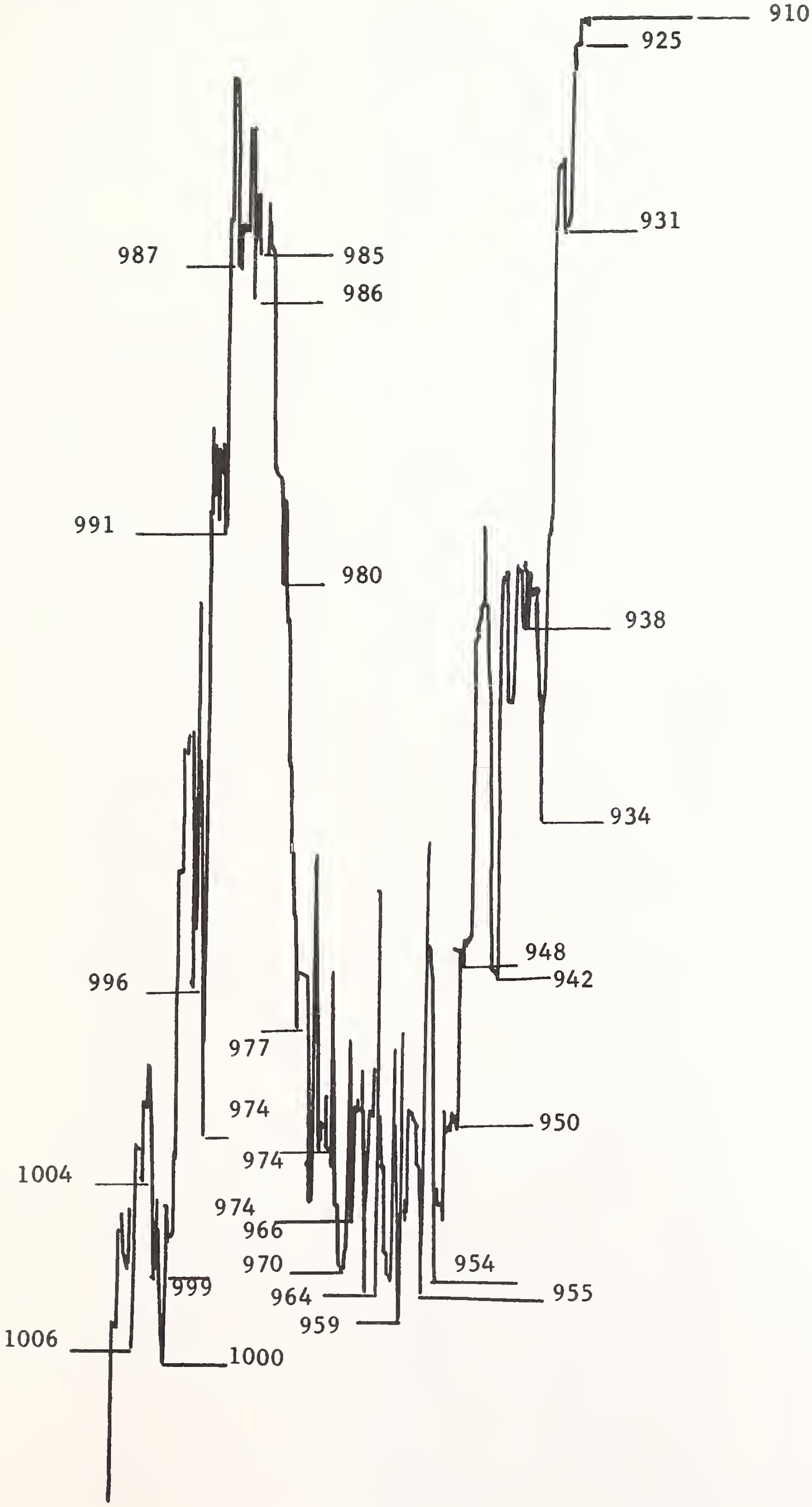




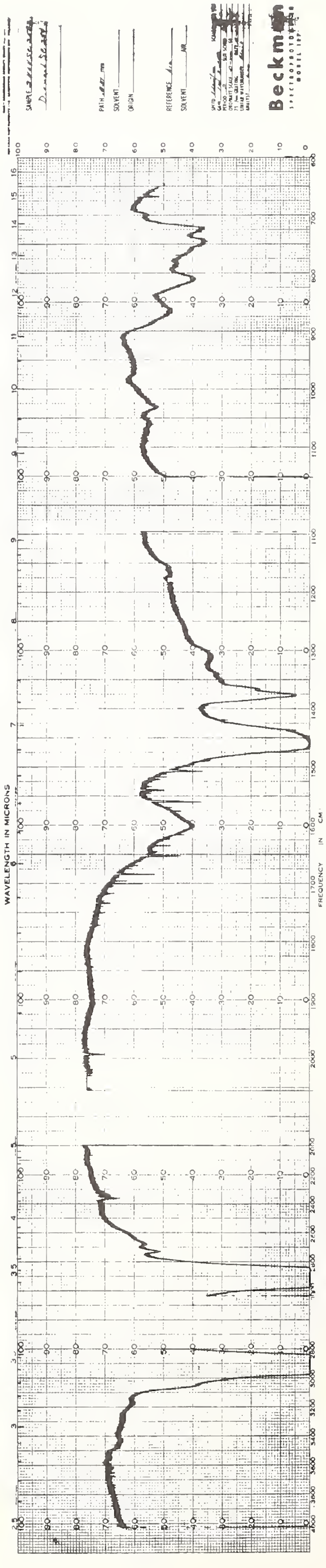
#2464 SC 2506
Diamond SC 250
Path .1 mm
Reference Air
Scale Selection 0-100
Gain 100 X.046
Scanning Speed 3.2 cm^{-1}/min.
Chart Speed 100 cm^{-1}/in.
Scale Expansion 17-25full
Period 8
Current .6
Date 2-4-64
Analyst - Lee

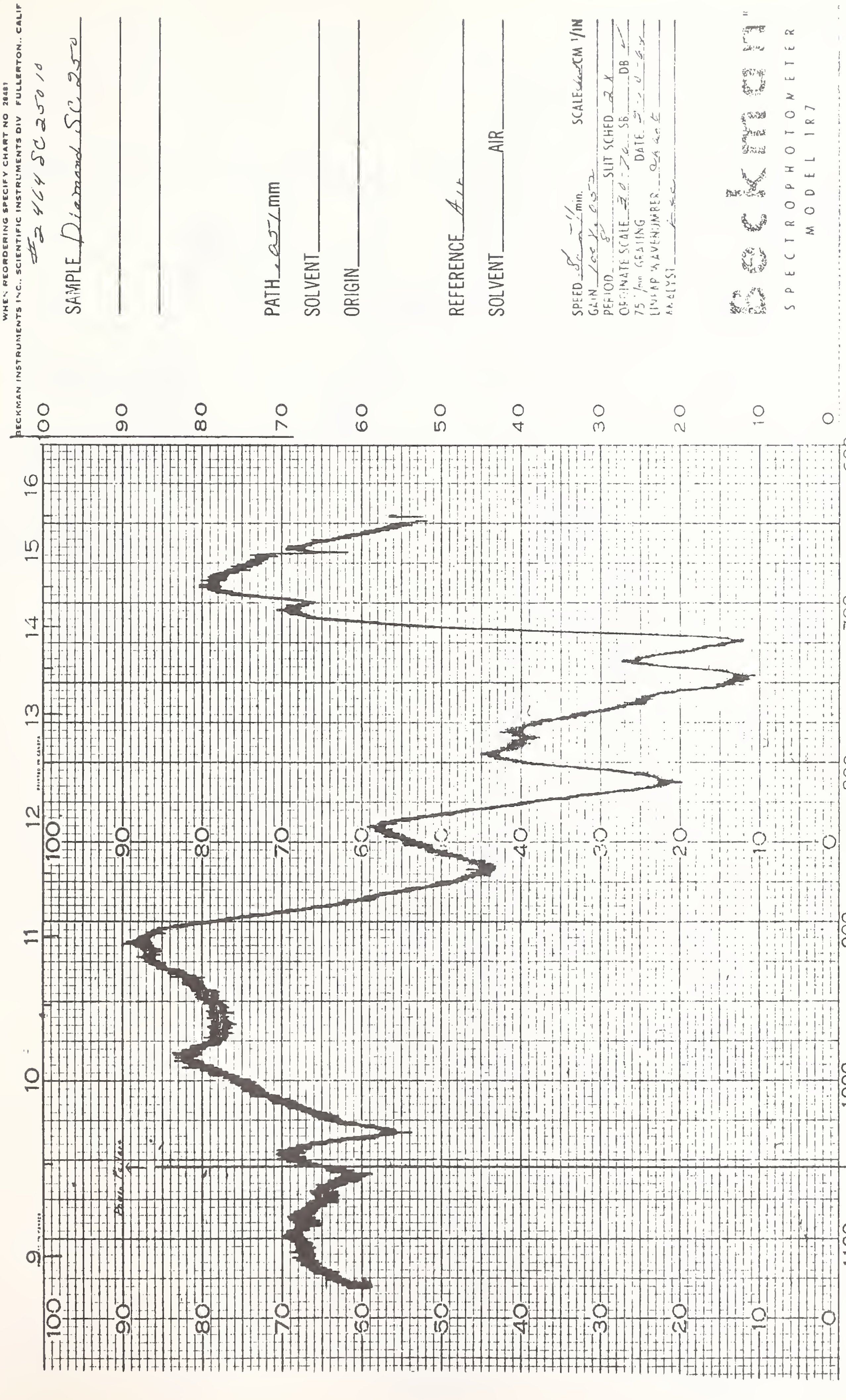


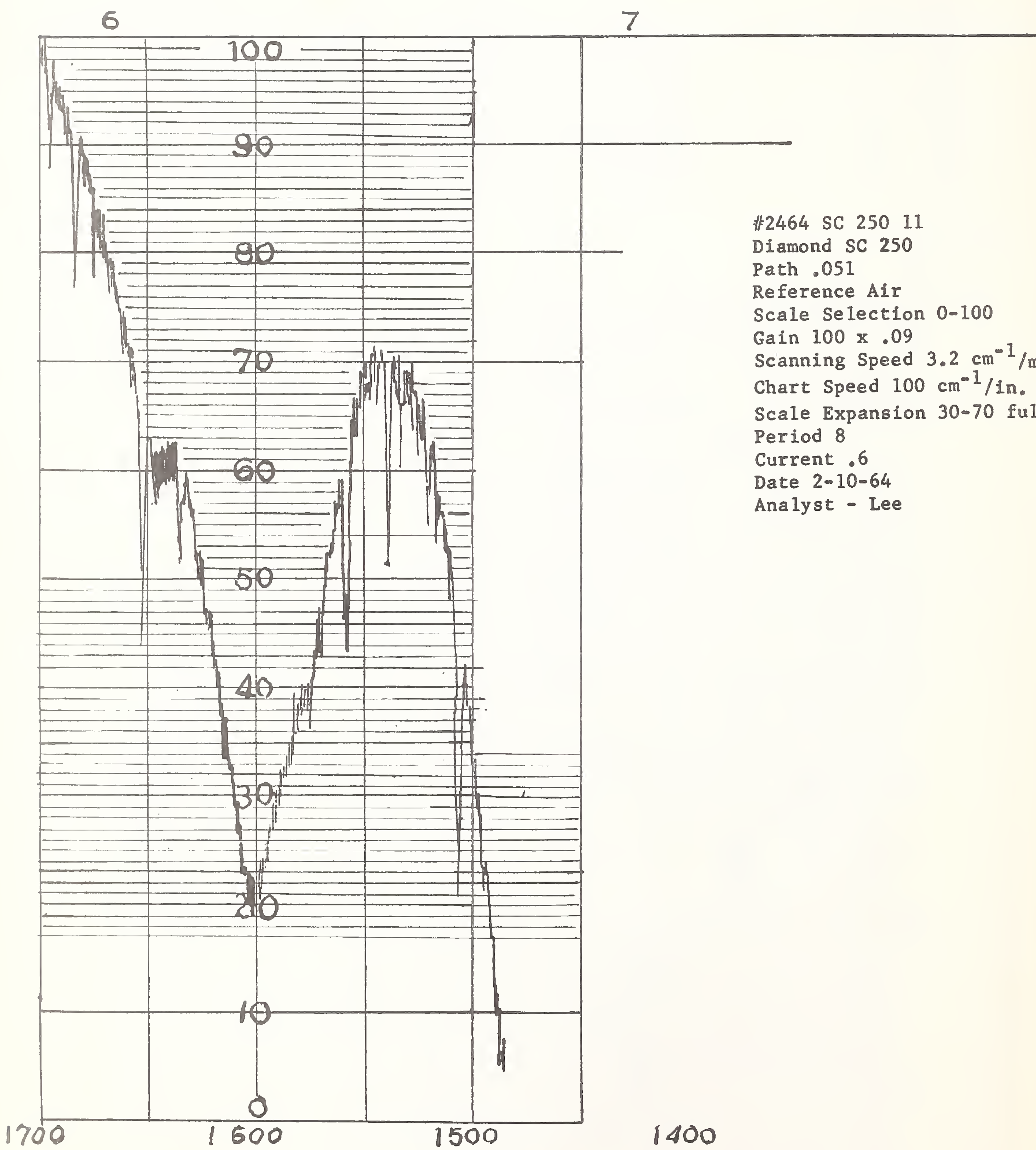
#2464 SC 2507
Diamond SC 250
Path .1 mm
Reference Air
Scale Selection 0-100
Gain 100 x .046
Scanning Speed 3.2 cm^{-1}/min.
Chart Speed 100 cm^{-1}/in.
Scale Expansion 20-30 full
Period 8
Current .6
Date 2-10-64
Analyst - Lee



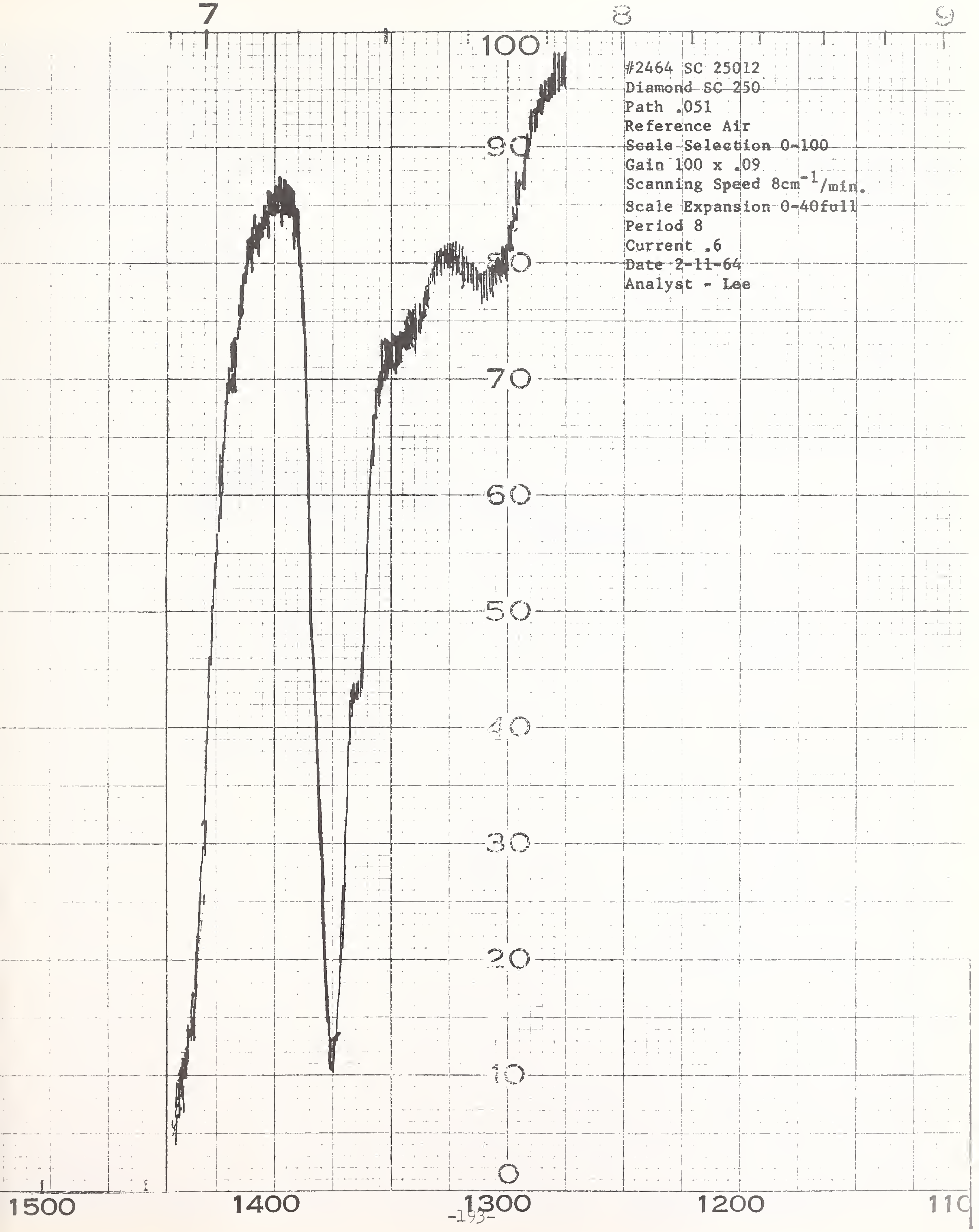
#2464 SC 2508
Diamond SC 250
Path .1 mm
Reference Air
Scale Selection 0-100
Gain 100 x .046
Scanning Speed 32 cm^{-1}/min.
Chart Speed 100 cm^{-1}/in.
Scale Expansion 20-30 full
Period 8
Current .6
Date 2-10-64
Analyst - Lee

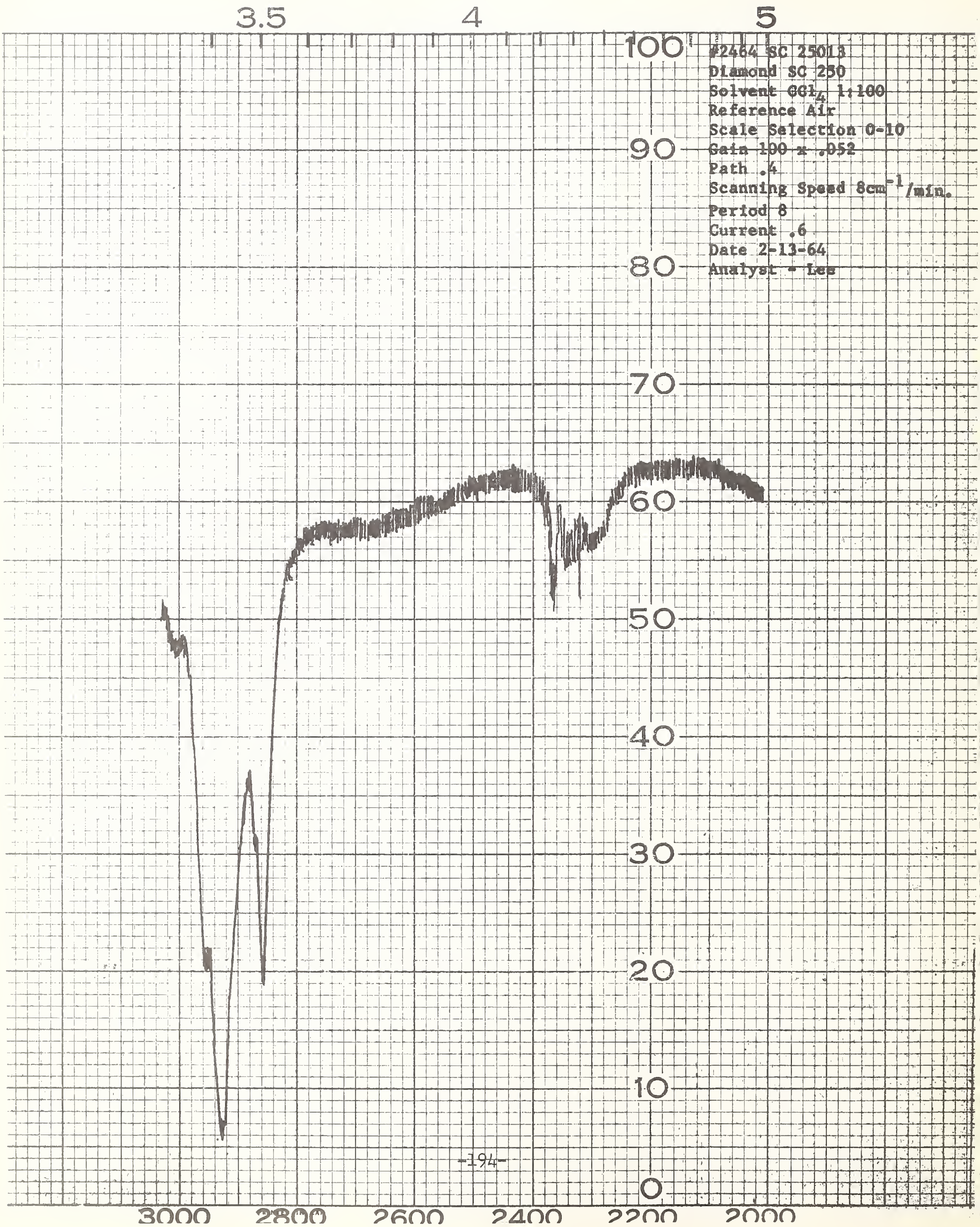

WAVELENGTH IN MICRONS
FREQUENCY IN CM
Beckman


WHEN REORDERING SPECIFY CHART NO 28481
BECKMAN INSTRUMENTS INC., SCIENTIFIC INSTRUMENTS DIV FULLERTON, CALIF
SAMPLE Diamond
PATH mm
SOLVENT
ORIGIN
REFERENCE Air
SOLVENT
AIR
Beckman
SPECTROPHOTOMETER
MODEL IR7

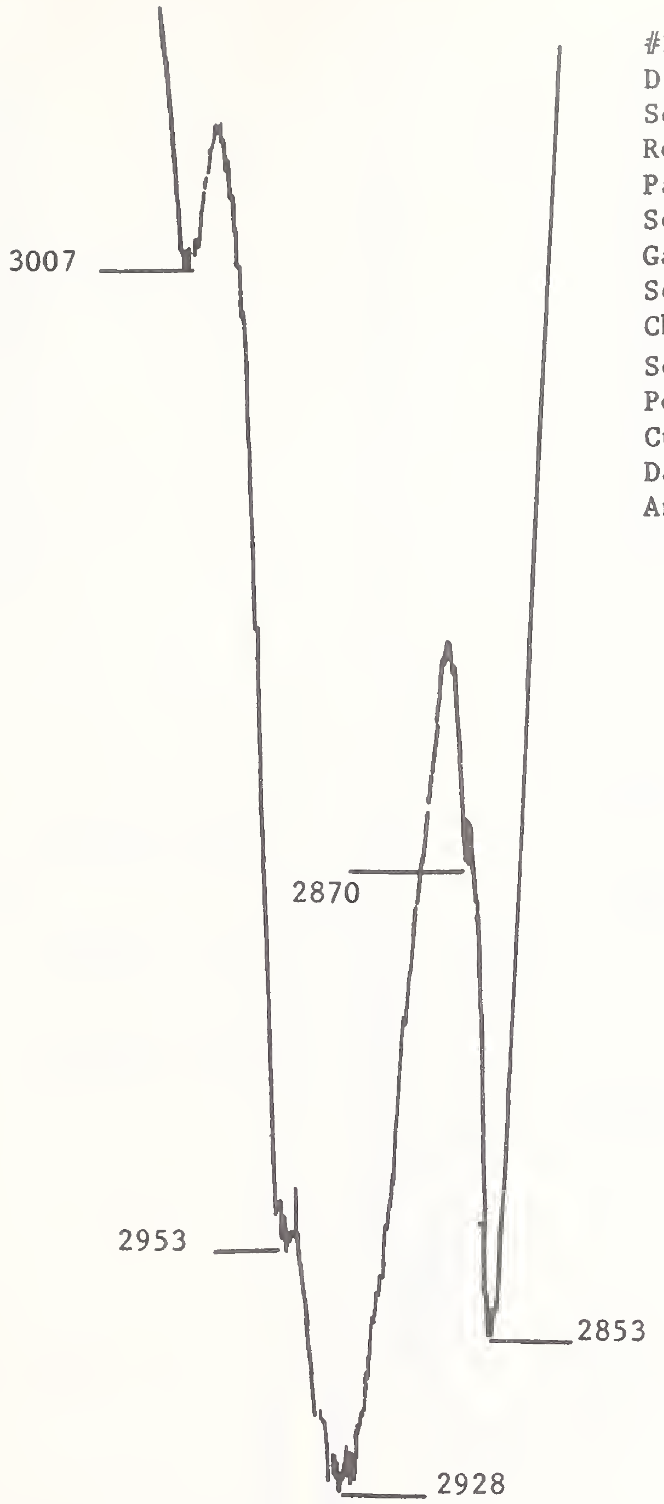


#2464 SC 250 11
Diamond SC 250
Path .051
Reference Air
Scale Selection 0-100
Gain 100 x .09
Scanning Speed 3.2 cm^{-1}/min.
Chart Speed 100 cm^{-1}/in.
Scale Expansion 30-70 full
Period 8
Current .6
Date 2-10-64
Analyst - Lee

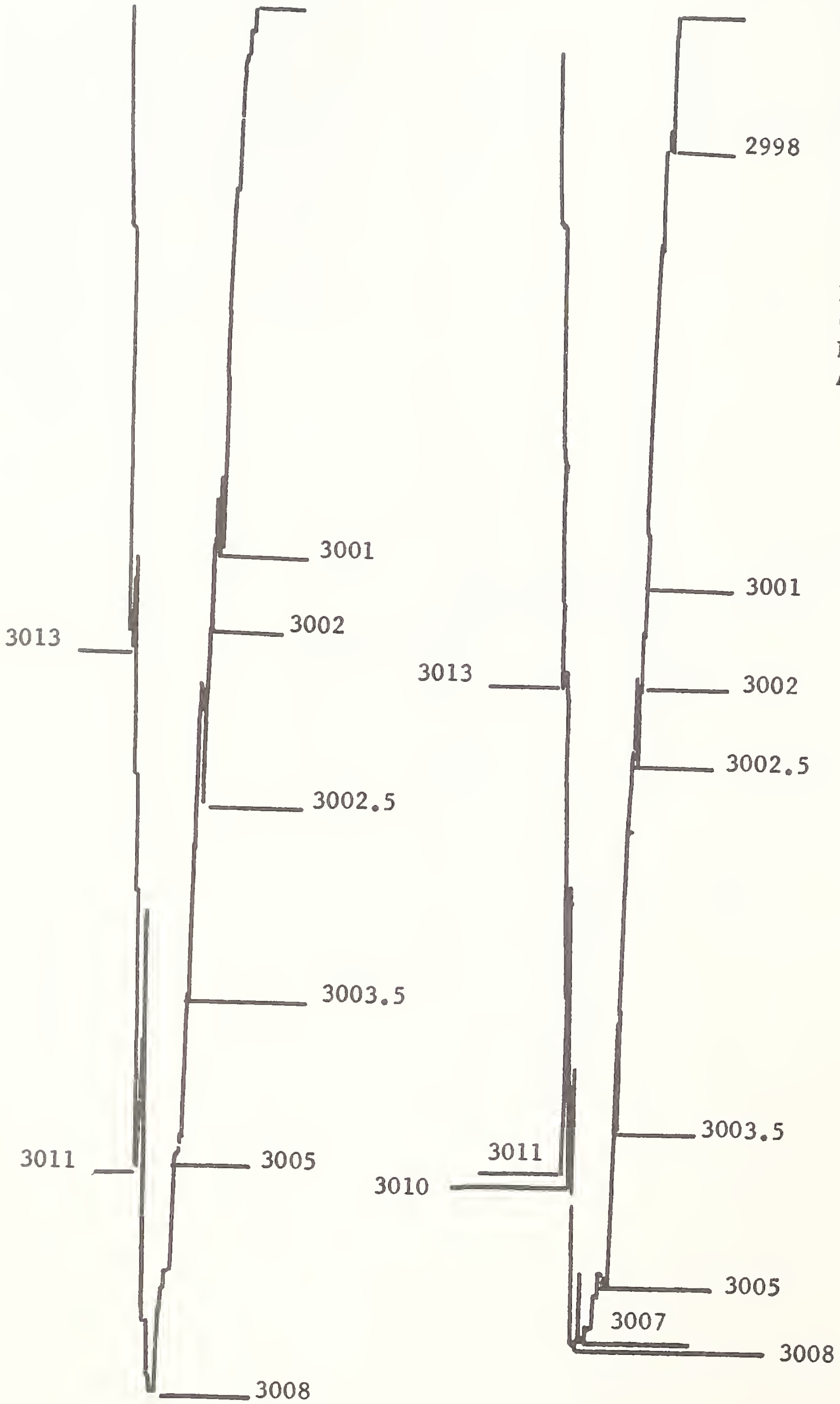

#2464 SC 25012
Diamond SC 250
Path .051
Reference Air
Scale Selection 0-100
Gain 100 x .09
Scanning Speed 8cm^{-1}/min.
Scale Expansion 0-40full
Period 8
Current .6
Date 2-11-64
Analyst - Lee
7
8
9
100
90
80
70
60
50
40
30
20
10
0
1500
1400
1300
1200
110



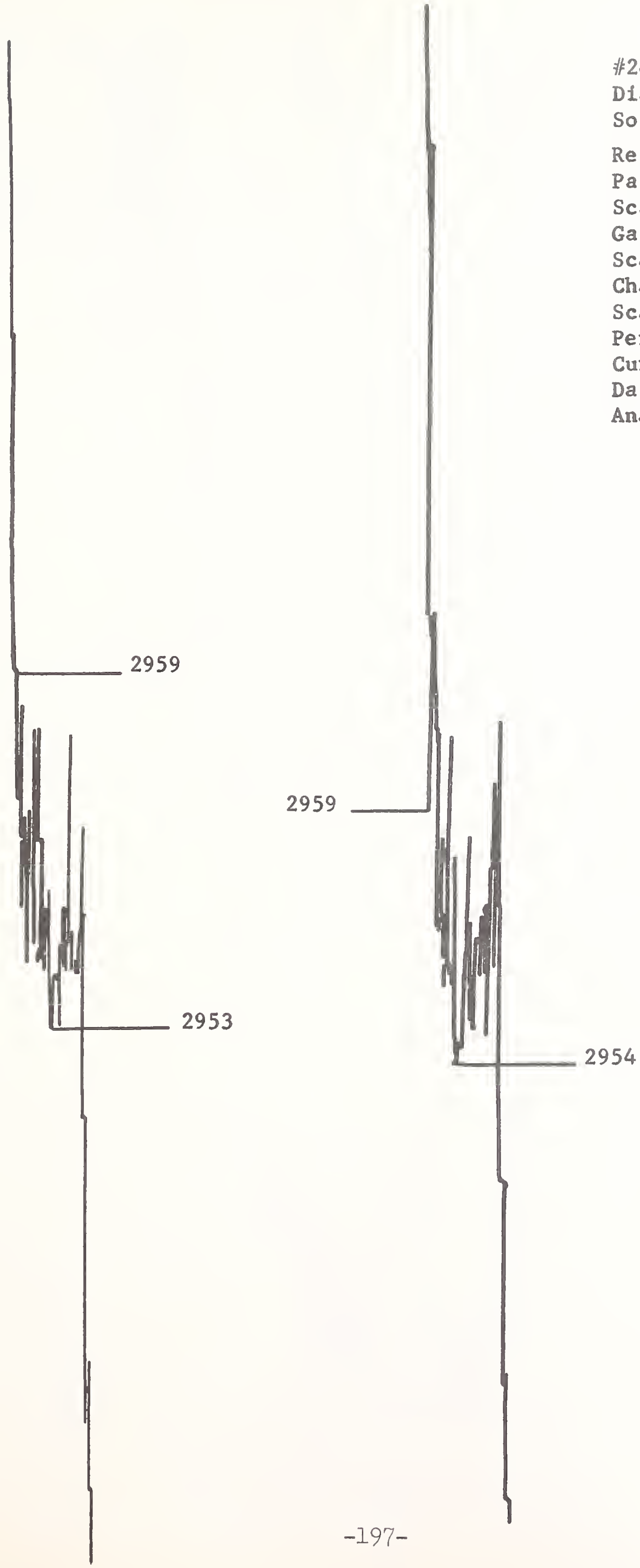
#2464 SC 25013
Diamond SC 250
Solvent CCl_4 1:100
Reference Air
Scale Selection 0-10
Gain 100 x .052
Path .4
Scanning Speed 8cm^{-1}/min.
Period 8
Current .6
Date 2-13-64
Analyst - Les
3.5
4
5
100
90
80
70
60
50
40
30
20
10
0
3000
2800
2600
2400
2200
2000
-194-



#2464 SC 25014
Diamond SC 250
Solvent CCl_4 1:100
Reference Air
Path .4
Scale Selection 0-100
Gain 100 x .052
Scanning Speed 3.2 cm^{-1}/min.
Chart Speed 100 cm^{-1}/in.
Scale Expansion 0-41 full
Period 8
Current .6
Date 2-13-64
Analyst - Lee



#2464 SC 25015
Diamond SC 250
Solvent CCl_4 1:100
Reference Air
Path .4
Scale Selection 0-100
Gain 100 x .052
Scanning Speed 13.2cm^{-1}/min.
Chart Speed 20cm^{-1}/in.
Scale Expansion 45-50 full
Period 32
Current .6
Date 2-13-64
Analyst - Lee



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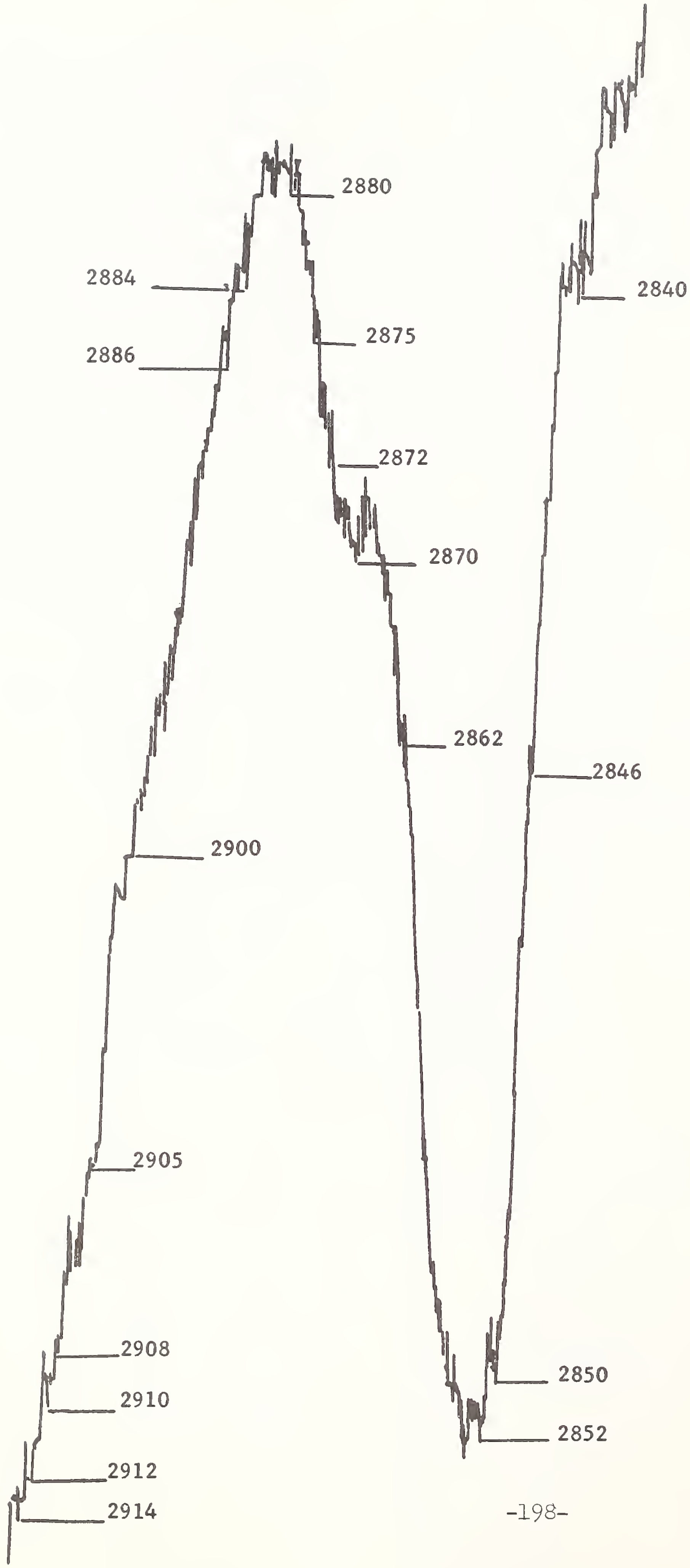
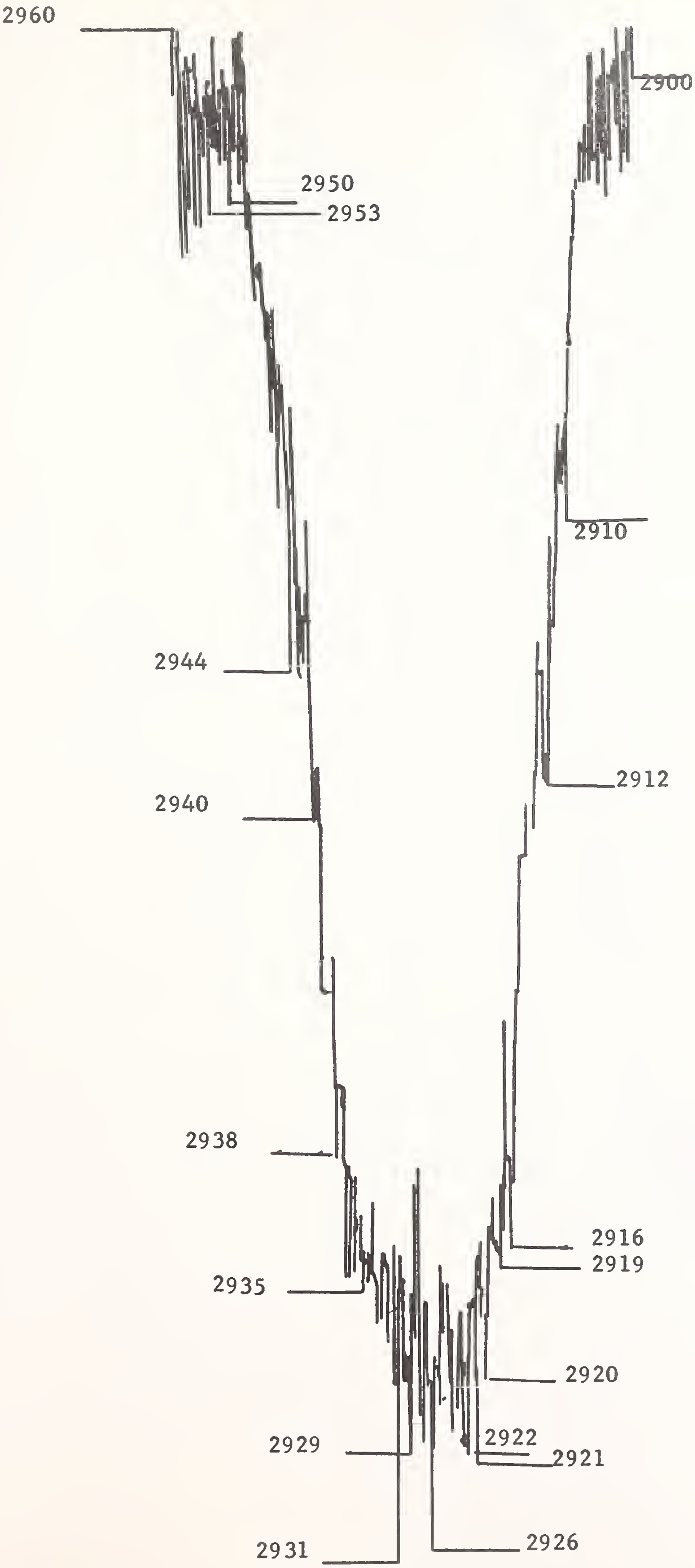
Diamond SC 250
Solvent CCl_4 1:100

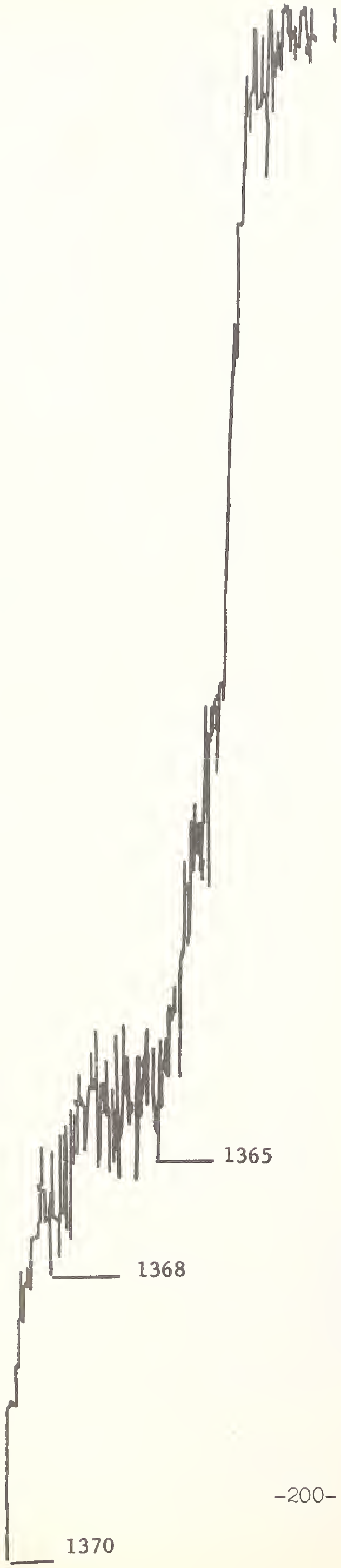
Reference Air
Path .4
Scale Selection 0-100
Gain 100 x .052
Scanning Speed 3.2cm^{-1}/min.
Chart Speed 20cm^{-1}/in.
Scale Expansion 18-22 full
Period 32
Current .6
Date 2-13-64
Analyst - Lee



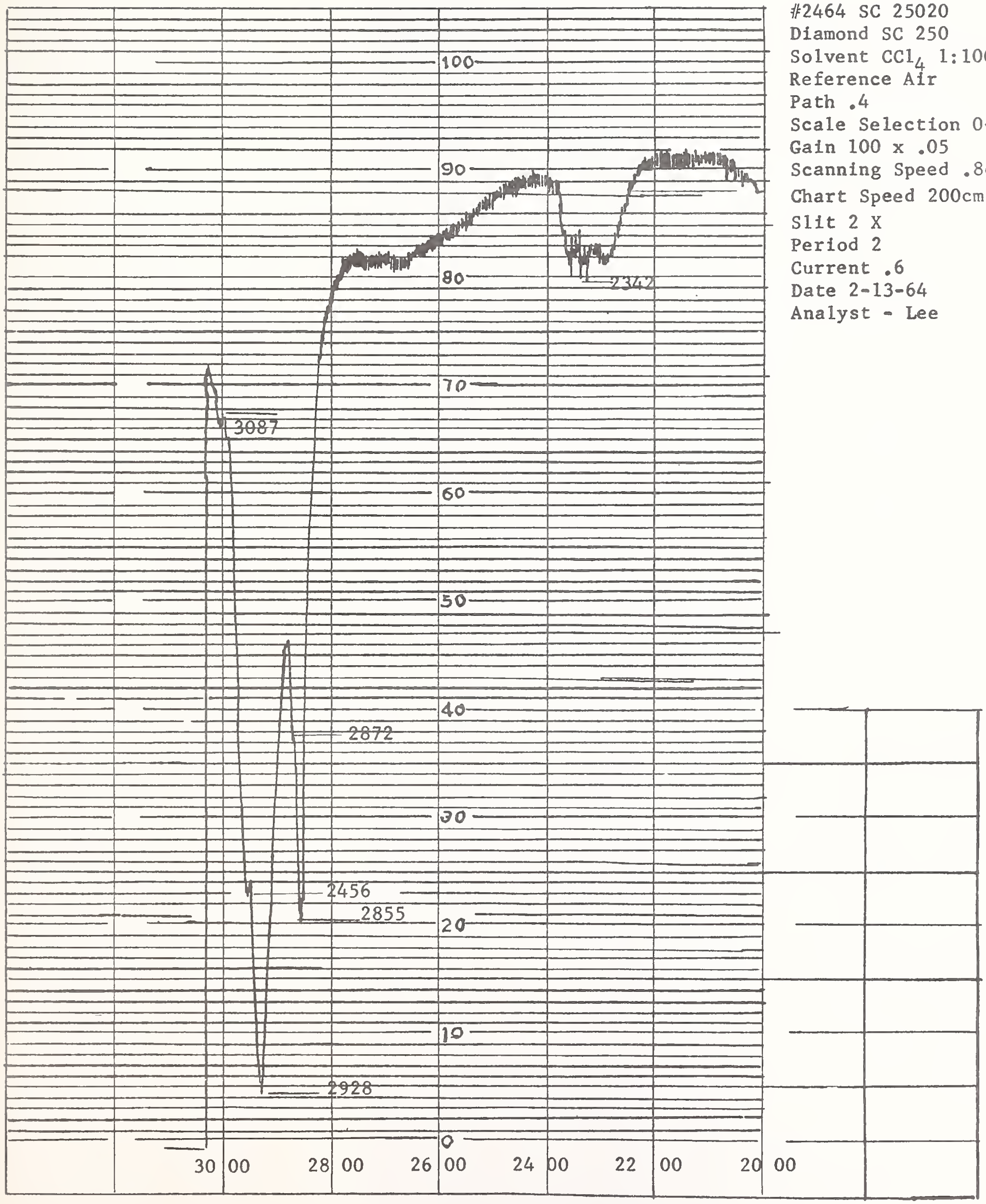
#2464 SC 25017
Solvent CCl_4 1:100
Reference Air
Path .4
Scale Selection 0-100
Gain 100 x .052
Scanning Speed 1.6cm^{-1}/min.
Chart Speed 20cm^{-1}/in.
Scale Expansion 15-40 full
Period 8
Current .6
Date 2-13-64
Analyst - Lee



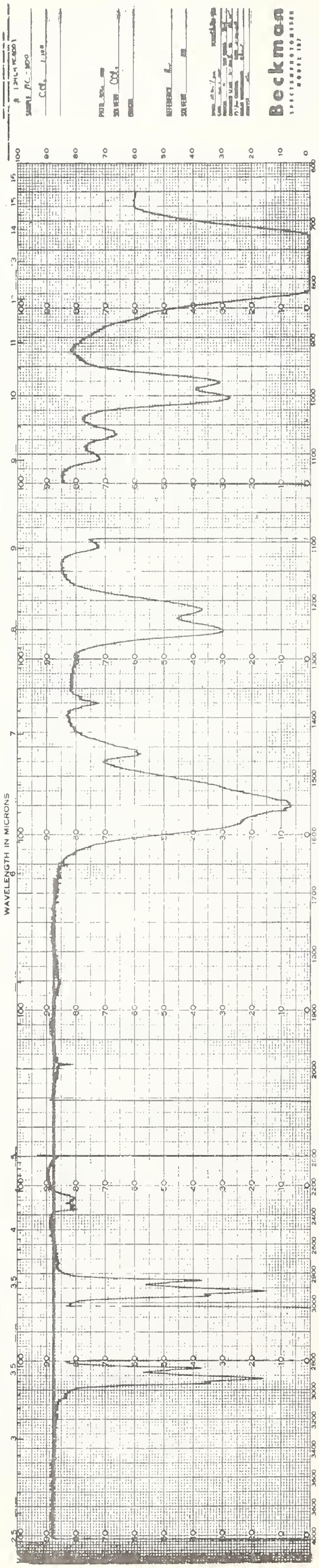
#2464 SC 25018
Diamond SC 250
Solvent CCl_4 1:100
Reference Air
Path .4
Scale Selection 0-100
Gain 100 x .052
Scanning Speed 1.6cm^{-1}/min.
Chart Speed 20cm^{-1}/in.
Scale Expansion 5-20 full
Period 8
Current .6
Date 2-13-64
Analyst - Lee

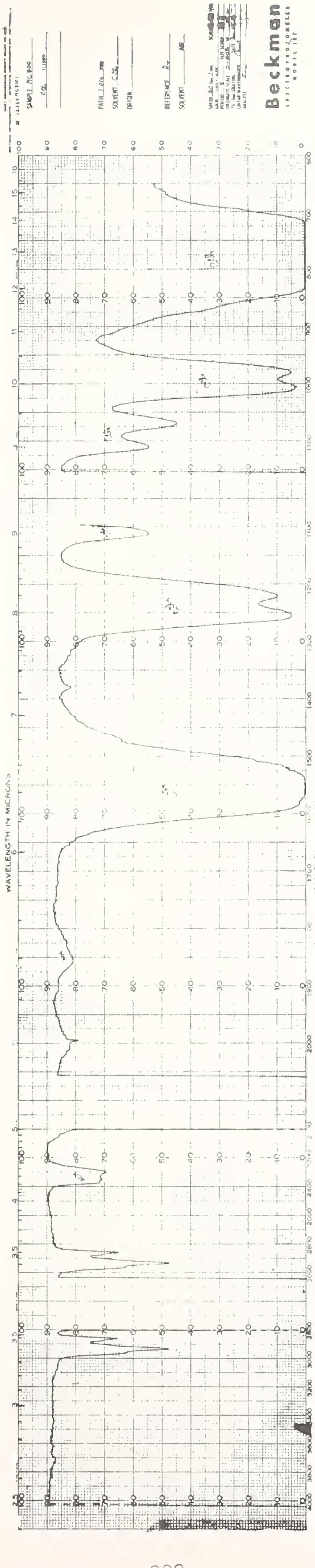


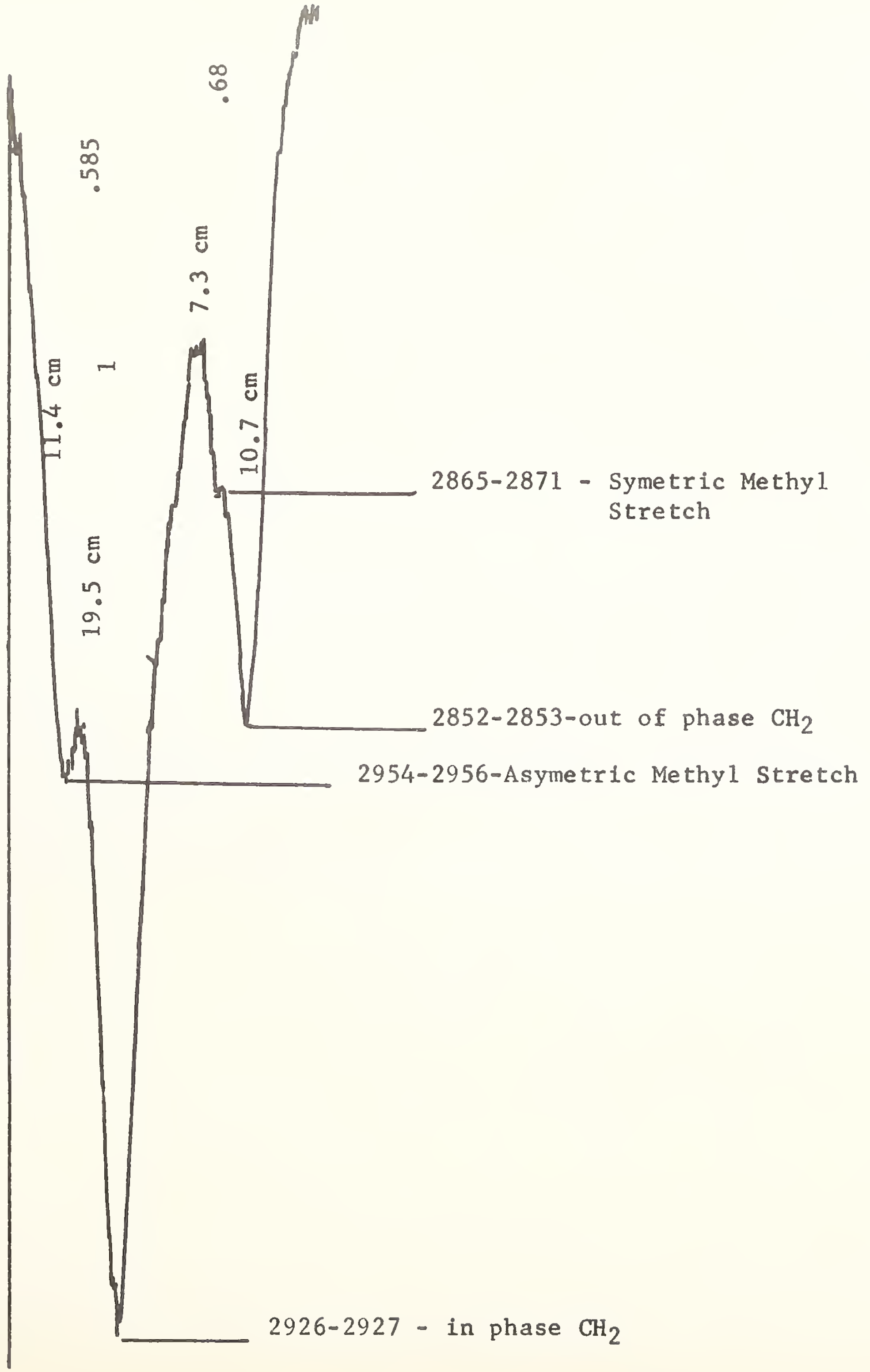
#2464 SC 25019
Diamond SC 250
Solvent CCl_4 1:100
Reference Air
Path .051 m m
Scale Selection 0-100
Gain 100 x .052
Scanning Speed 1.6 cm^{-1}/min.
Chart Speed 20 cm^{-1}/in.
Scale Expansion 40-45 full
Period 8
Current .6
Date 2-13-64
Analyst - Lee



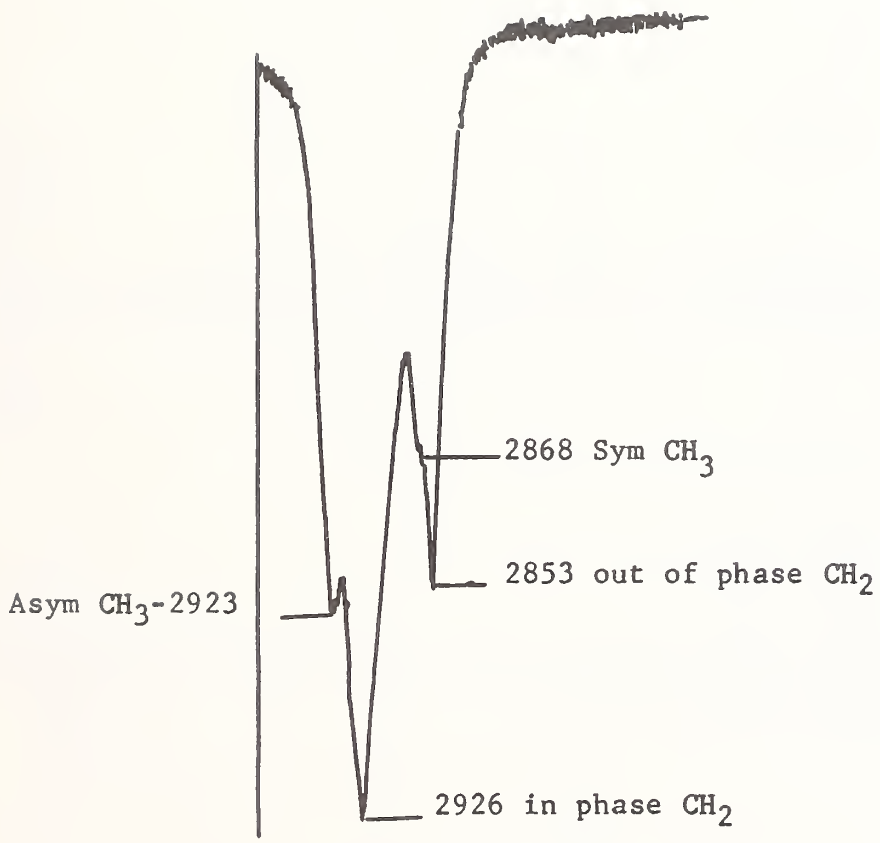
#2464 SC 25020
Diamond SC 250
Solvent CCl_4 1:100
Reference Air
Path .4
Scale Selection 0-100%
Gain 100 x .05
Scanning Speed .8cm $^{-1}$/min.
Chart Speed 200cm $^{-1}$/in.
Slit 2 X
Period 2
Current .6
Date 2-13-64
Analyst - Lee


WAVELENGTH IN MICRONS
FREQUENCY IN CM
Beckman

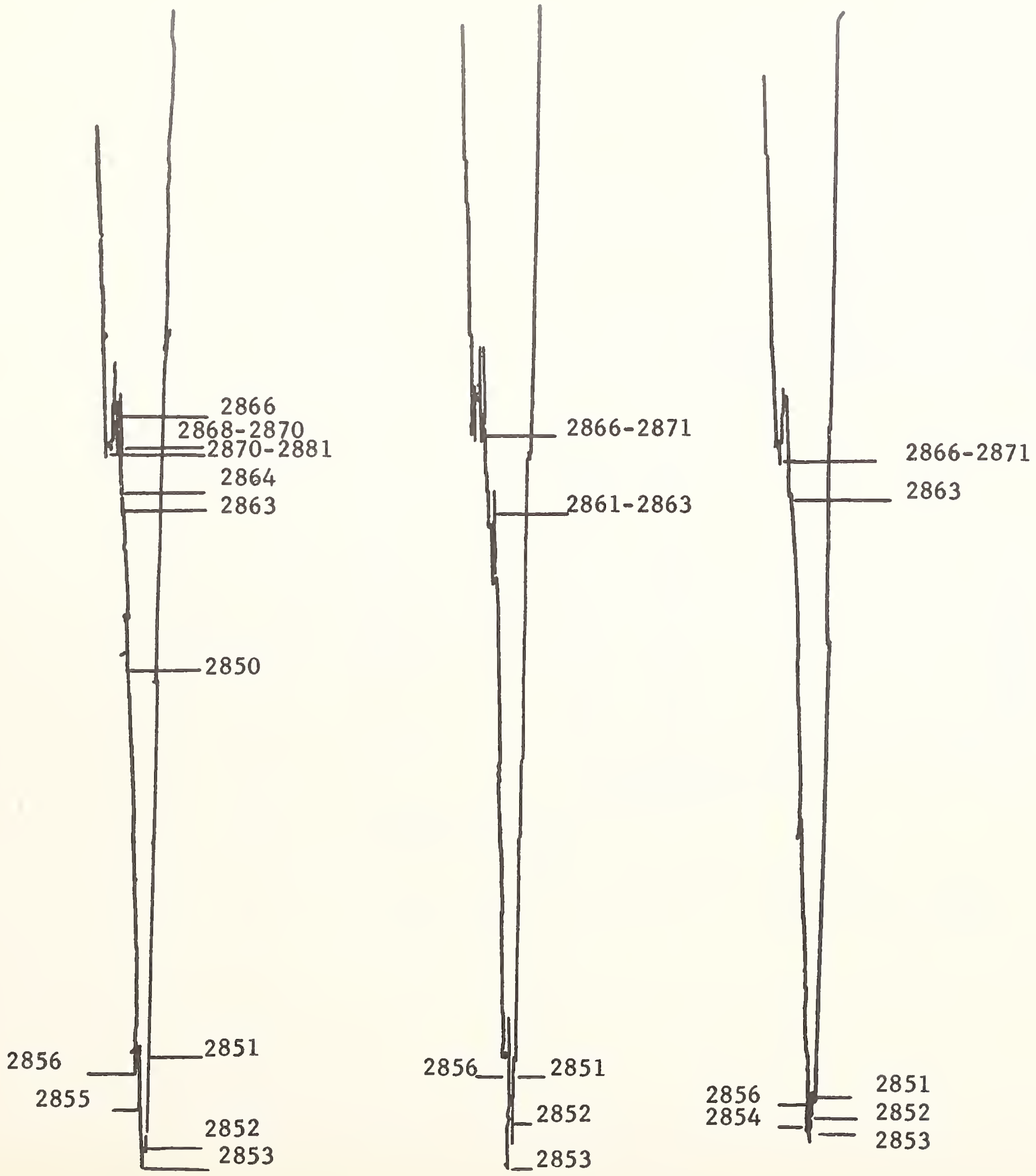

Beckman
WAVELENGTH IN MICRONS
FREQUENCY IN CM⁻¹



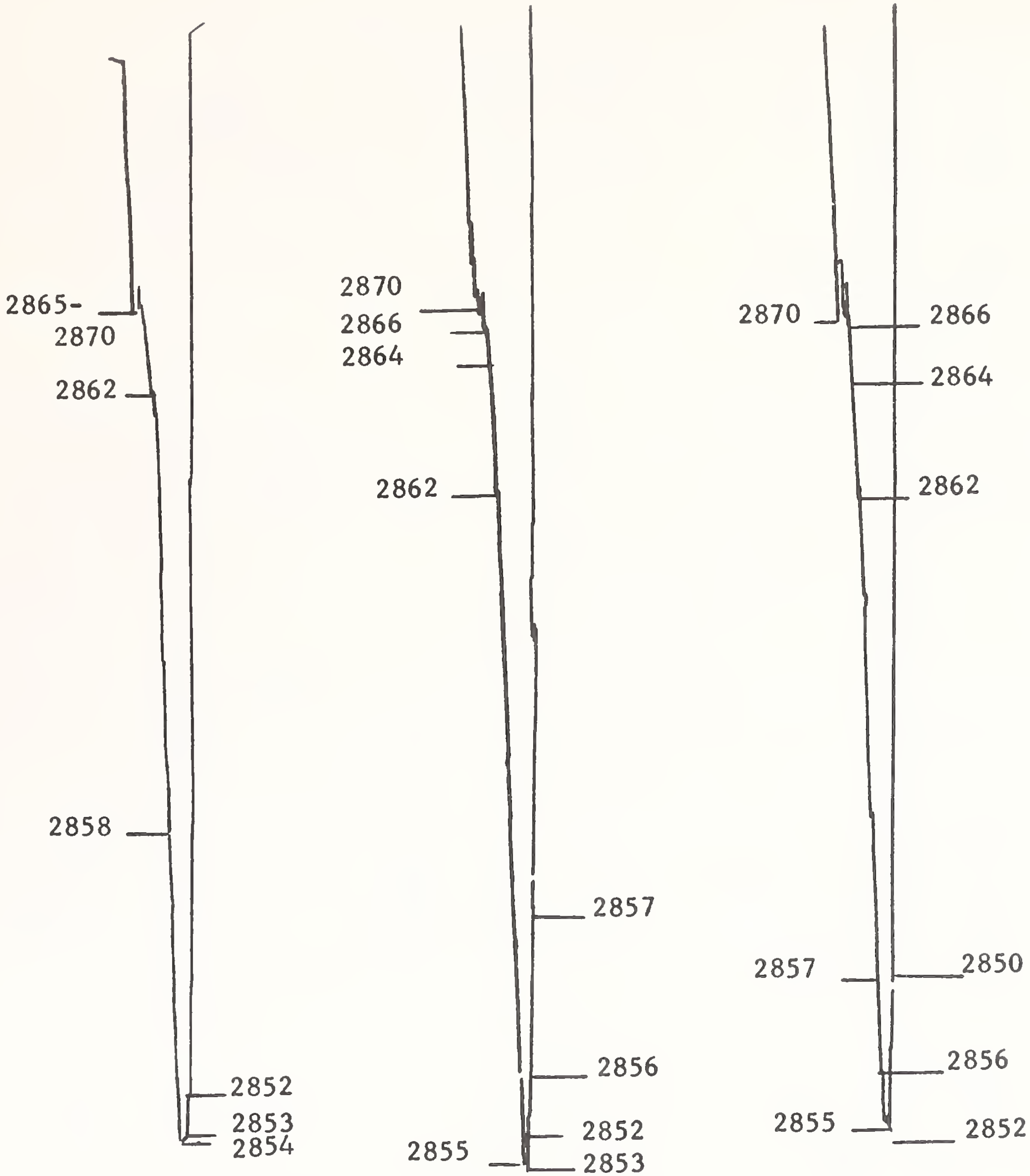
#12364 MC 8002
MC-800(1:1000
CCl_4 (
Path 1:016 m m
Reference Air
D B
Selection 5/3 X
Period 8
Current 0.6
Scale Selection 0-100%
Gain 100 x .038
Scanning Speed 1.6 cm^{-1}/min.
Scale Contract Off
Scale Expansion 35-60 full
Auto Out
Chart Speed 100 cm^{-1}/in.
Analyst - Lee



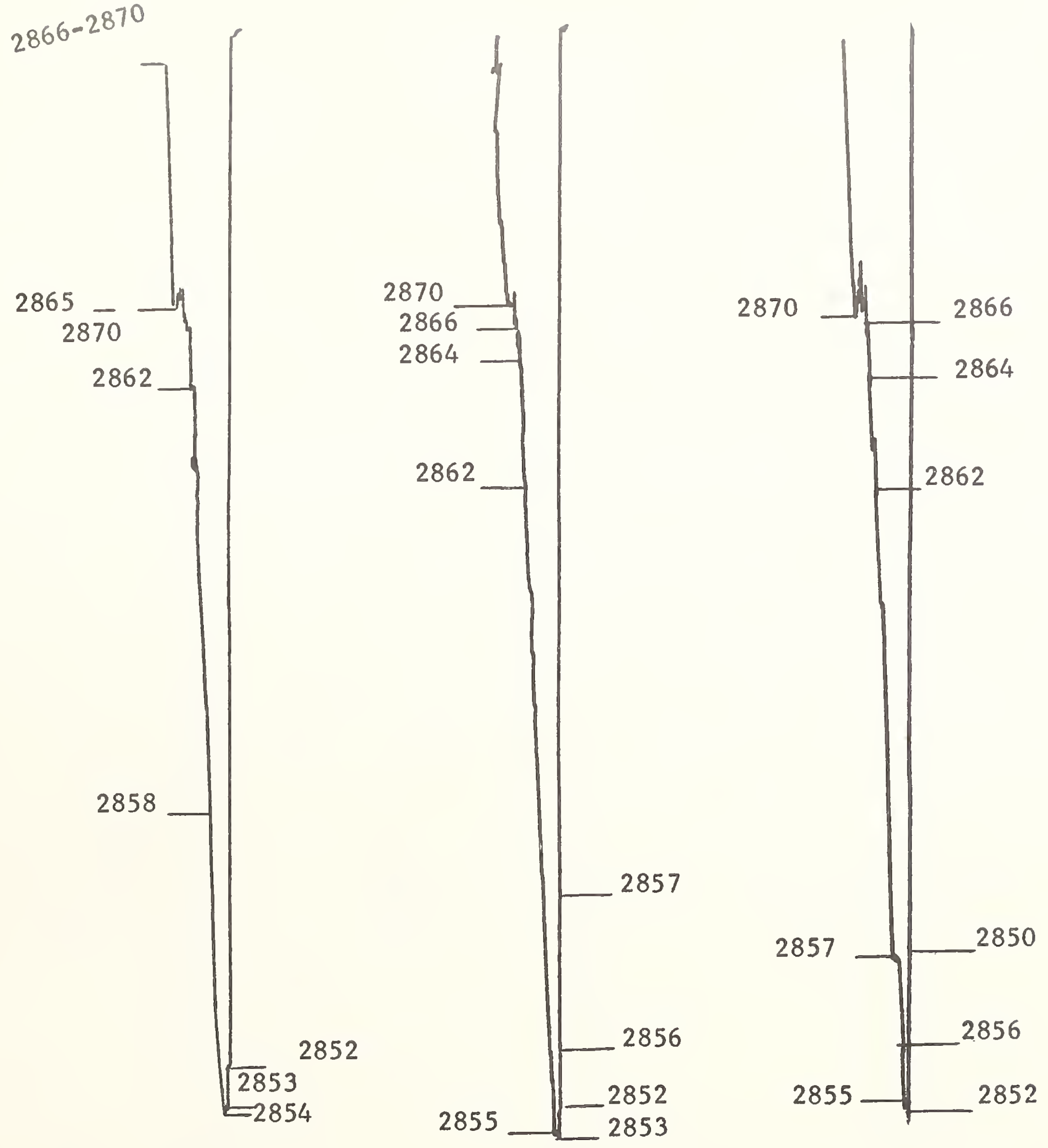
#12464 MC 8002
MC-800(1:100
CCl_4 (
Glower Current .6
Path 0.406 mm
Reference Air
Double Beam
Selection 5/3 X
Period 2
Scale Selection 0-100%
Gain 100 x .038
Scanning Speed 1.6cm^{-1}/min.
Scale Contract Off
Scale Expansion 10-80 full
Auto Out
Chart Speed 100 cm^{-1}/in.
Analyst - Lee



#12364 MC 8003
MC-800(1:1000
CCl_4 (
Glower Current .6
Scale Contract - Off
Scale Selection 0-100%
Gain 100 x .038
Double Beam
Selection 5/3 X
Period 8
Scale Expansion 12-10 full
Auto Out
Scanning Speed 1.6cm^{-1}/min.
Gear 50cm^{-1}/in.
Analyst - Lee

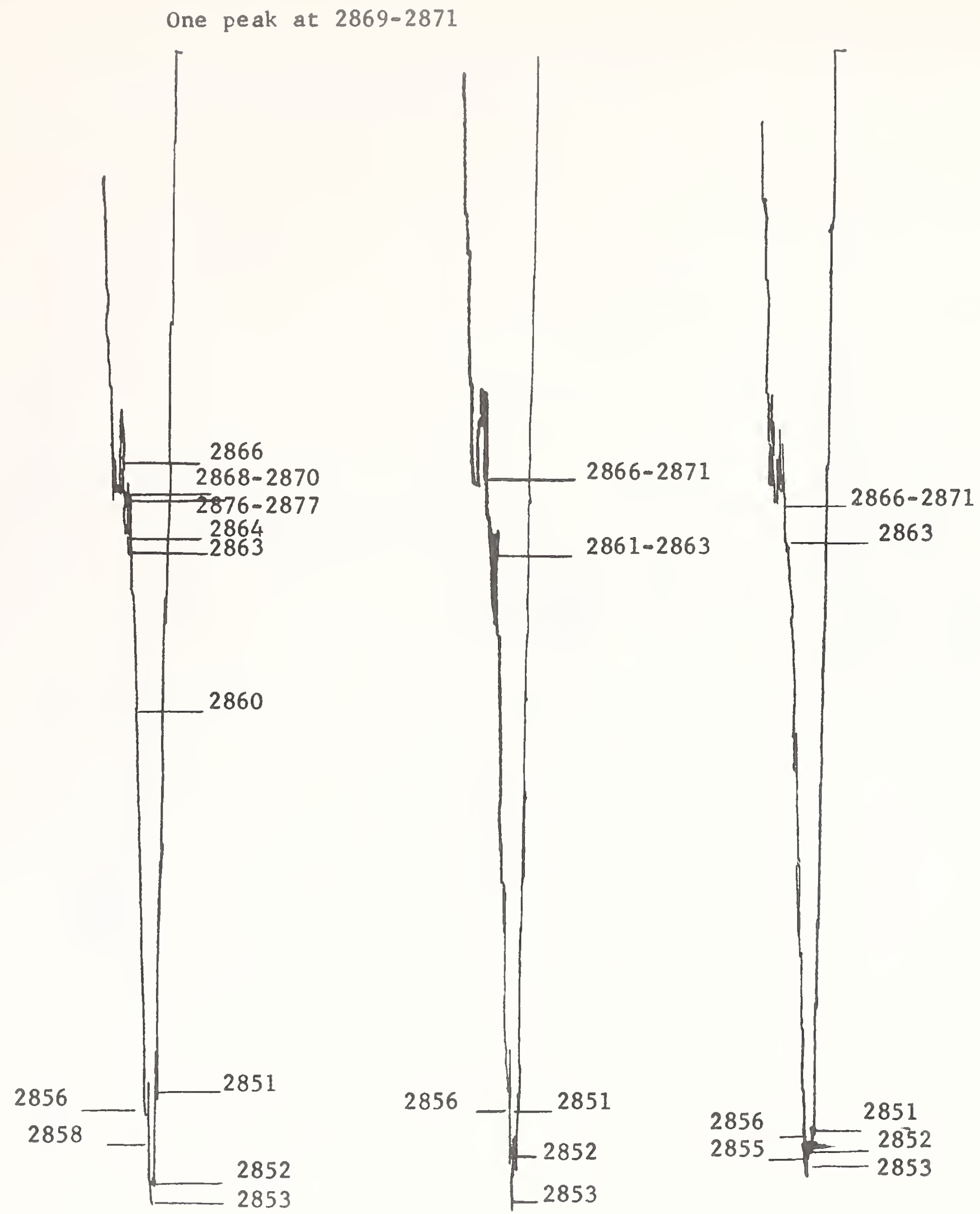


#12464 MC 8003
MC-800(1:100
CCl_4 (
Path 0.406 mm
Reference Air
Double Beam
Selection 5/3 x
Period 8
Current .6
Scale Selection 0-100%
Gain 100 x .038
Scanning Speed 1.6cm^{-1}/min.
Scale Contract Off
Scale Expansion 20-40 full
Auto Out
Chart Speed 50cm^{-1}/in.
Analyst - Lee



#12464 MC 8003
MC-800 (1:100
CCl_4 (
Path 0.406 mm
Reference Air
Double Beam
Selection 5/3x
Period 8
Current .6
Scale Selection 0-100%
Gain 100 x .038
Scanning Speed 16cm $^{-1}$/min.
Scale Contract Off
Scale Expansion 20-40 full
Auto Out
Chart Speed 50cm $^{-1}$/in.
Analyst - Lee

Out of phase
CH_2

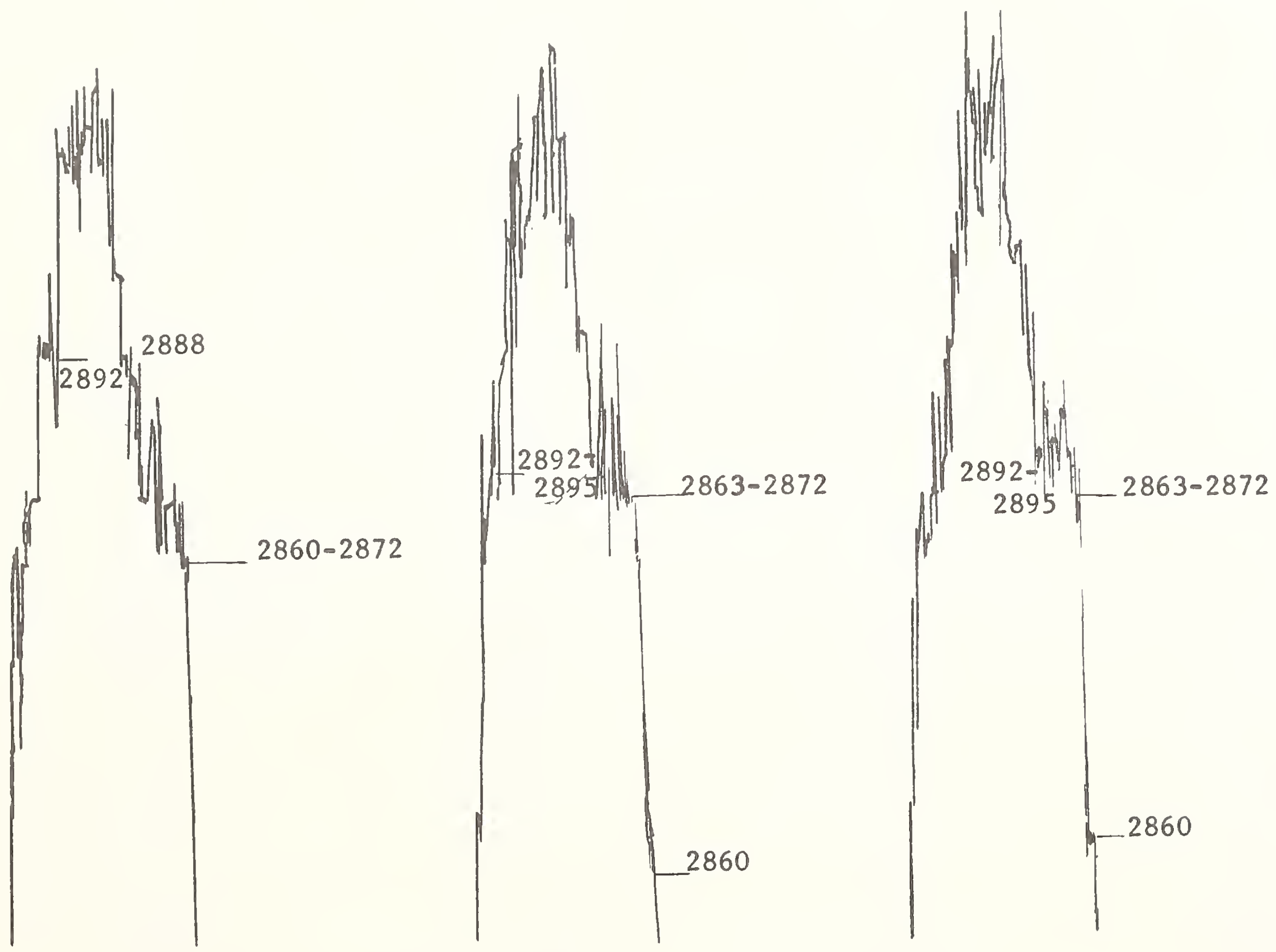


#12364 MC 8003
MC 800 (1:1000
CCl_4 (
Glower Current .6
Scale Contract - Off
Scale Selection 0-100%
Gain 100 x .038
Double Beam
Selection 5/3 x
Period 8
Scale Expansion 12-10 full
Auto Out
Scanning Speed 1.6cm $^{-1}$/min.
Gear 50cm $^{-1}$/in.
Analyst - Lee

Out of phase

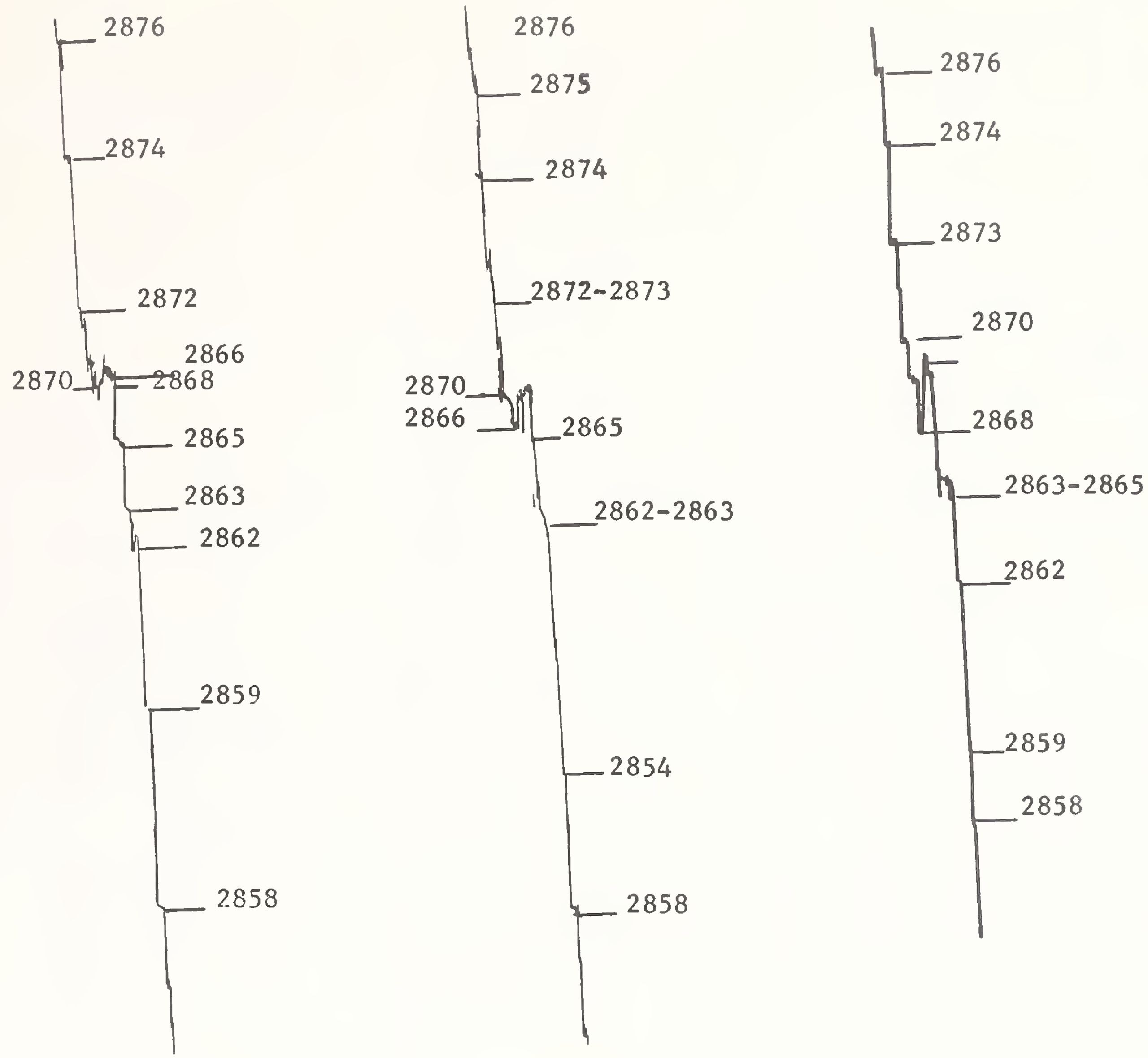
CH_2

One peak 2892 - CH



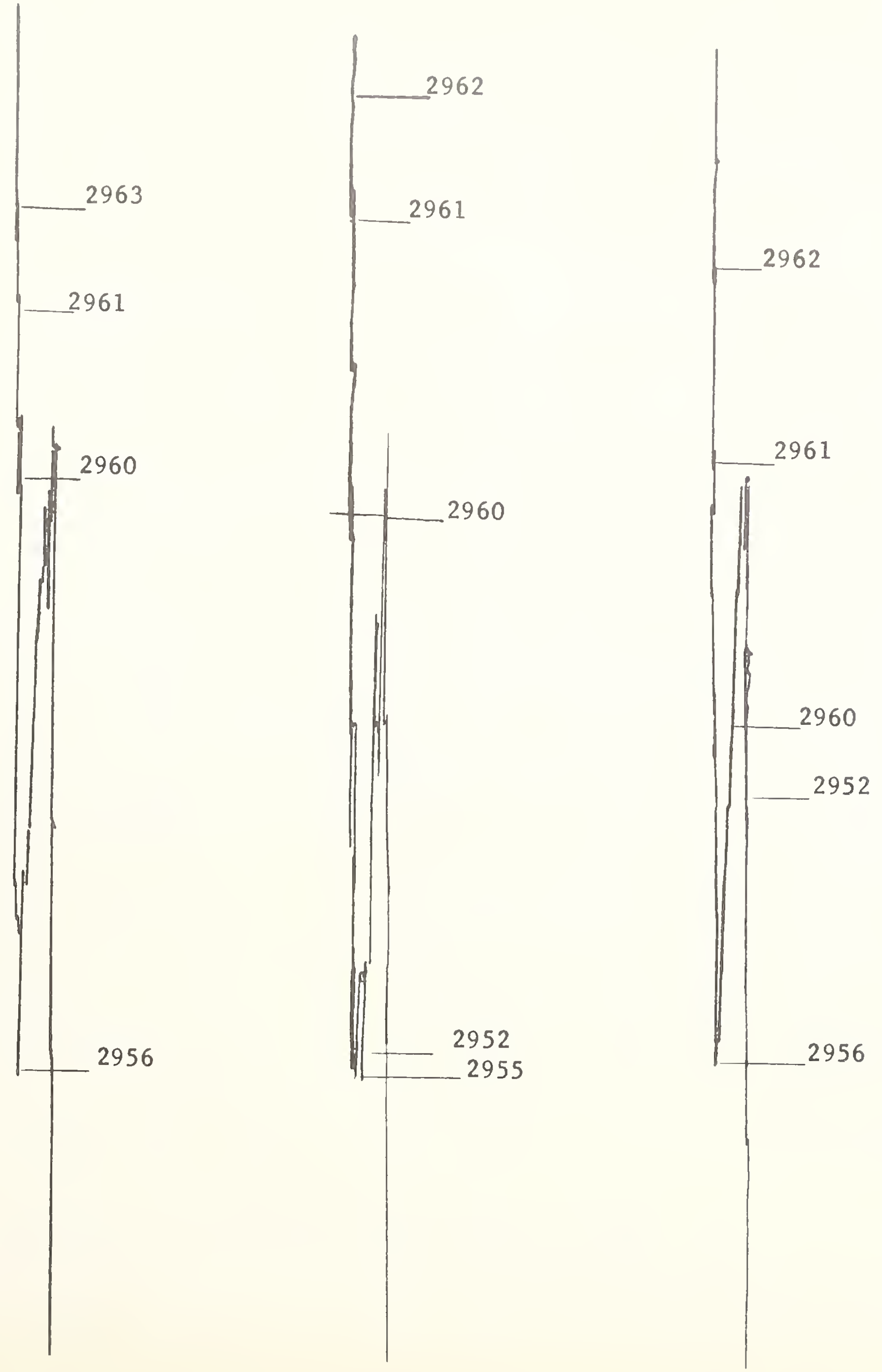
#12364 MC 8004
MC 800 (1:1000
CCl_4 (
Glower Current .6
Scale Contract Off
Scale Selection 0-100%
Gain 100 x .038
Double Beam
Selection 5/3x
Period 8
Scale Expansion (12-16) full plus
Auto Out
Scanning Speed .8cm^{-1}/min.
Gear 20cm^{-1}/in.
Analyst - Lee

One peak at an average wave number of 2868



#12464 MC 8004
MC 800 (1:100
CCl_4 (
Path 0.406 mm
Reference Air
Double Beam
Selection 5/3 x
Period 8
Current .6
Scale Selection 0-100%
Gain 100 x .038
Scanning Speed 1.6cm $^{-1}$/min.
Scale Contract Off
Scale Expansion 25-35 full
Auto Out
Chart Speed 20cm $^{-1}$/in.
Analyst - Lee

Symmetrical CH_3



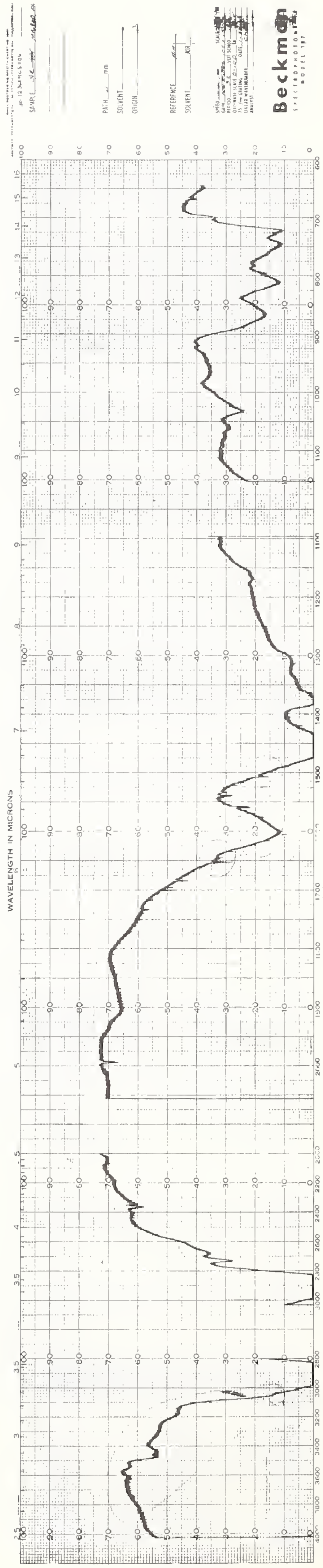
#12364 MC 8005
MC - 800
CCl_4

Glower Current .6
Scale Contract - Off
Scale Selection 0-100%
Gain 100 x .038
Double Beam
Selection 5/3 x
Period 8
Scale Expansion 30-40 full
Auto Out
Scanning Speed 1.6cm $^{-1}$/min.
Gear 100 cm^{-1}/in.
Analyst - Lee

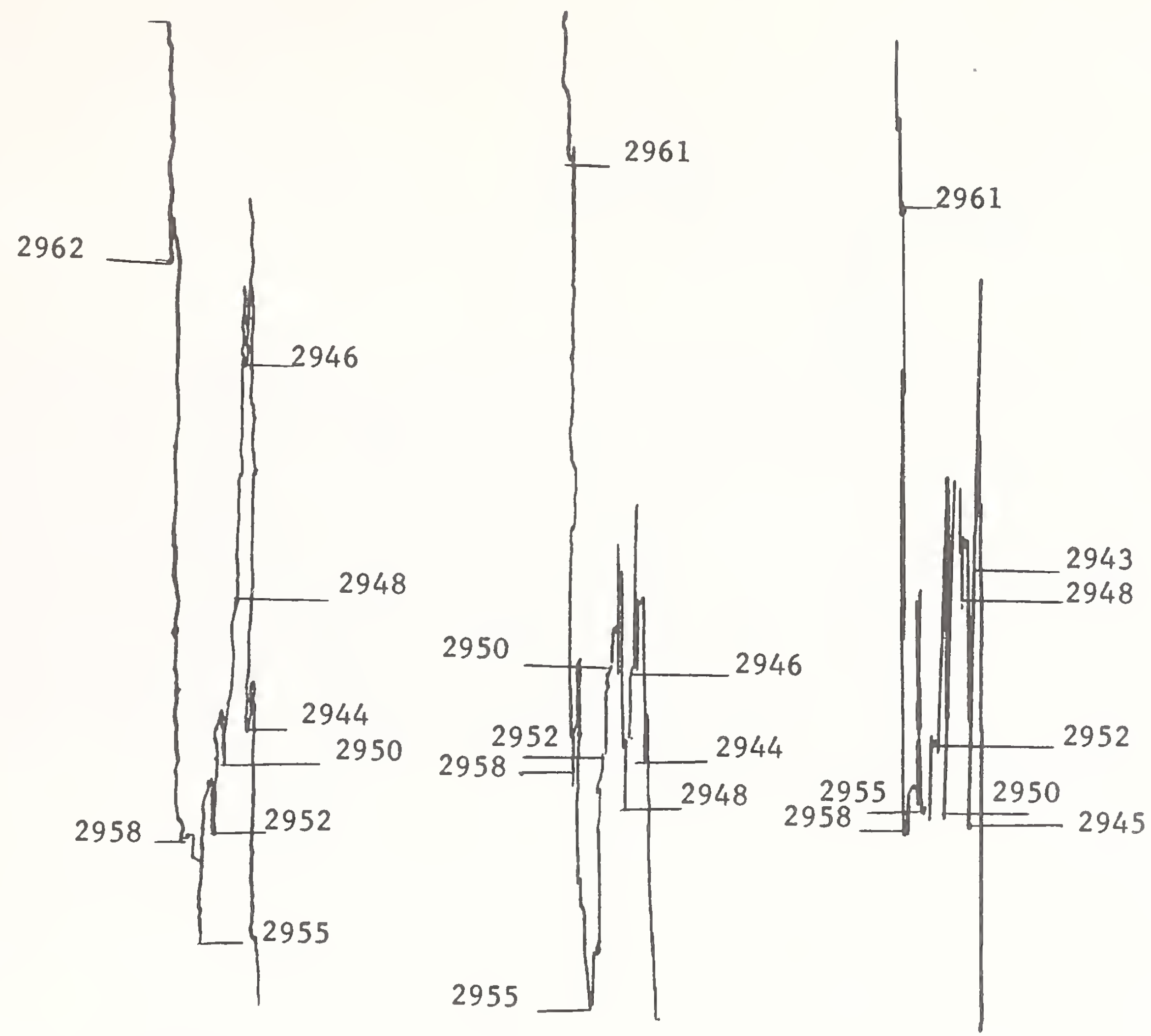
Asymmetrical CH_3

#12464 MC 8005
MC 800 (1:100
CCl_4 (
Path 0.406 mm
Reference Air
Double Beam
Selection 5/3 X
Period 8
Current .6
Scale Selection 10-20 full
Gain 100 x .038
Scanning Speed 1.6 cm $^{-1}$/min.
Scale Contract Off
Auto Out
Chart Speed 20cm $^{-1}$/in.
Analyst - Lee

In Phase CH_2


WAVELENGTH IN MICRONS
FREQUENCY
Beckman

There are two main peaks in this region 2955 & 2958

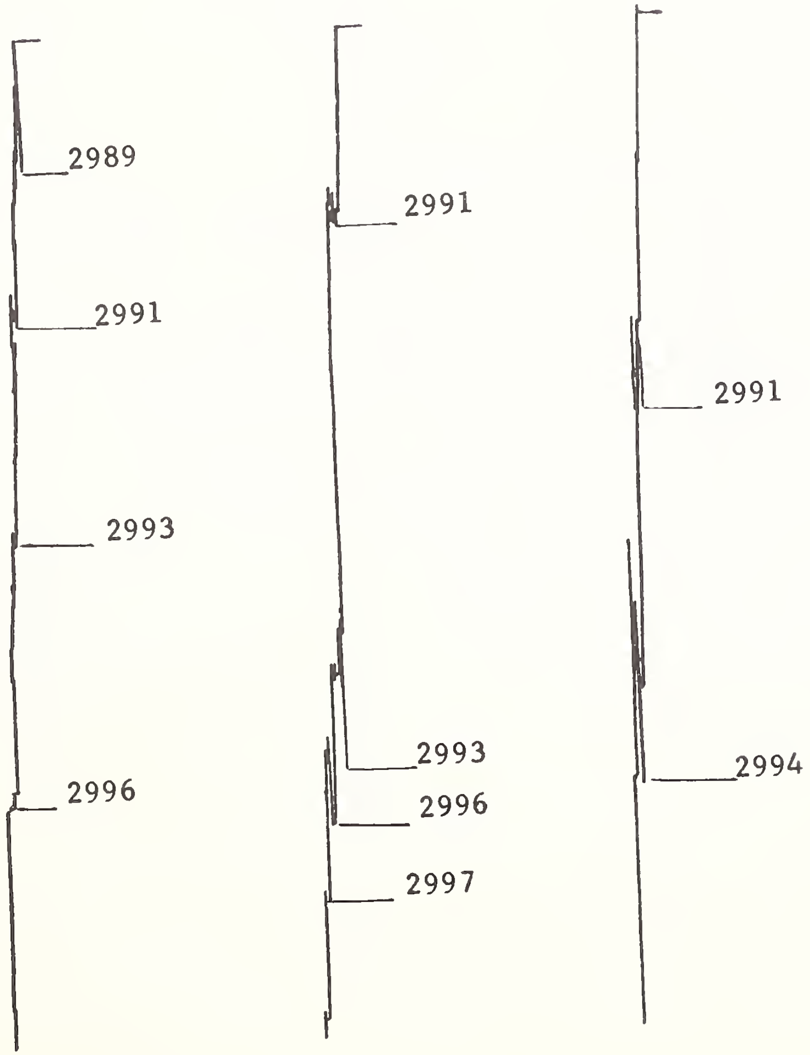


#12464 MC 8006
MC 800 (1:100
CCl_4 (
Glower Current .6
Path 0.406 mm
Reference Air
Double Beam
Selection 5/3 X
Period 2
Scale Selection 0-100%
Gain 100 x .038
Scanning Speed 1.6cm $^{-1}$/min.
Scale Contract Off
Scale Expansion 10-80 full
Auto Out
Chart Speed 100cm $^{-1}$/in.
Analyst - Lee

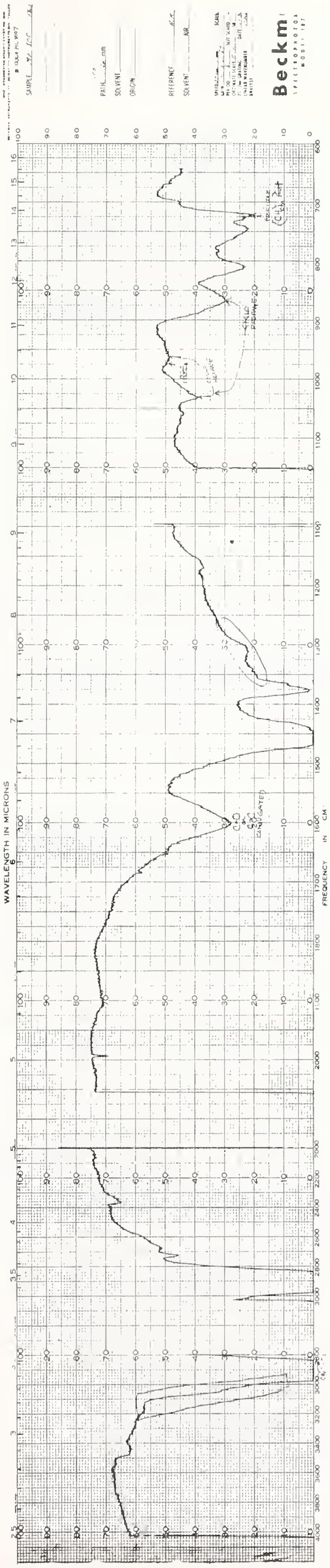
Asymmetrical CH_3

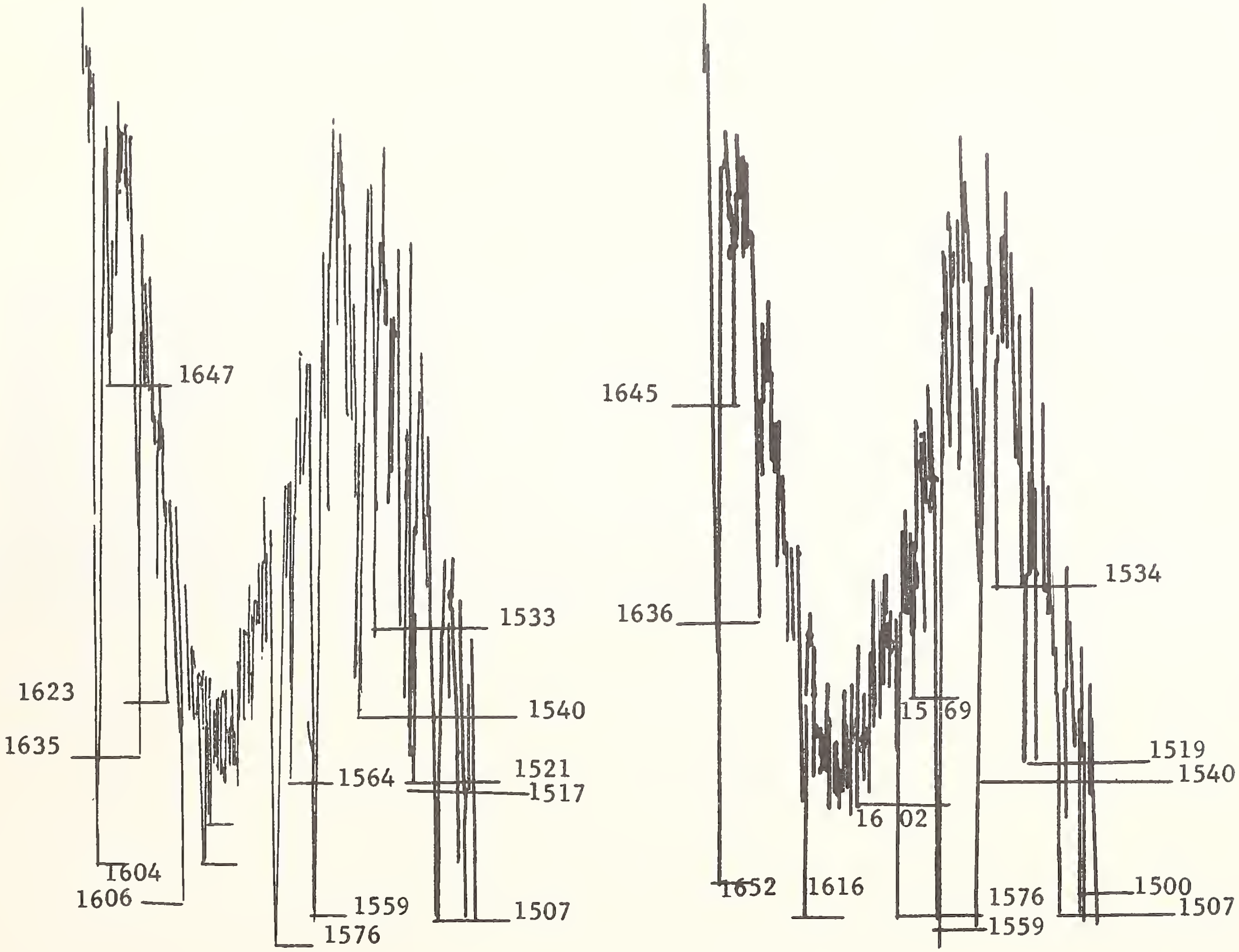
Average Range 2989 - 2996

#12664 MC 8007
MC 800 (1:100
CCl_4 (
Glower Current .6
Path 0.406 mm
Reference Air
Double Beam
Selection 5/3 X
Period 2
Scale Selection 0-100%
Scanning Speed 16cm $^{-1}$/min.
Scale Contract Off
Auto Out
Chart Speed 100cm $^{-1}$/min.
Analyst - Lee

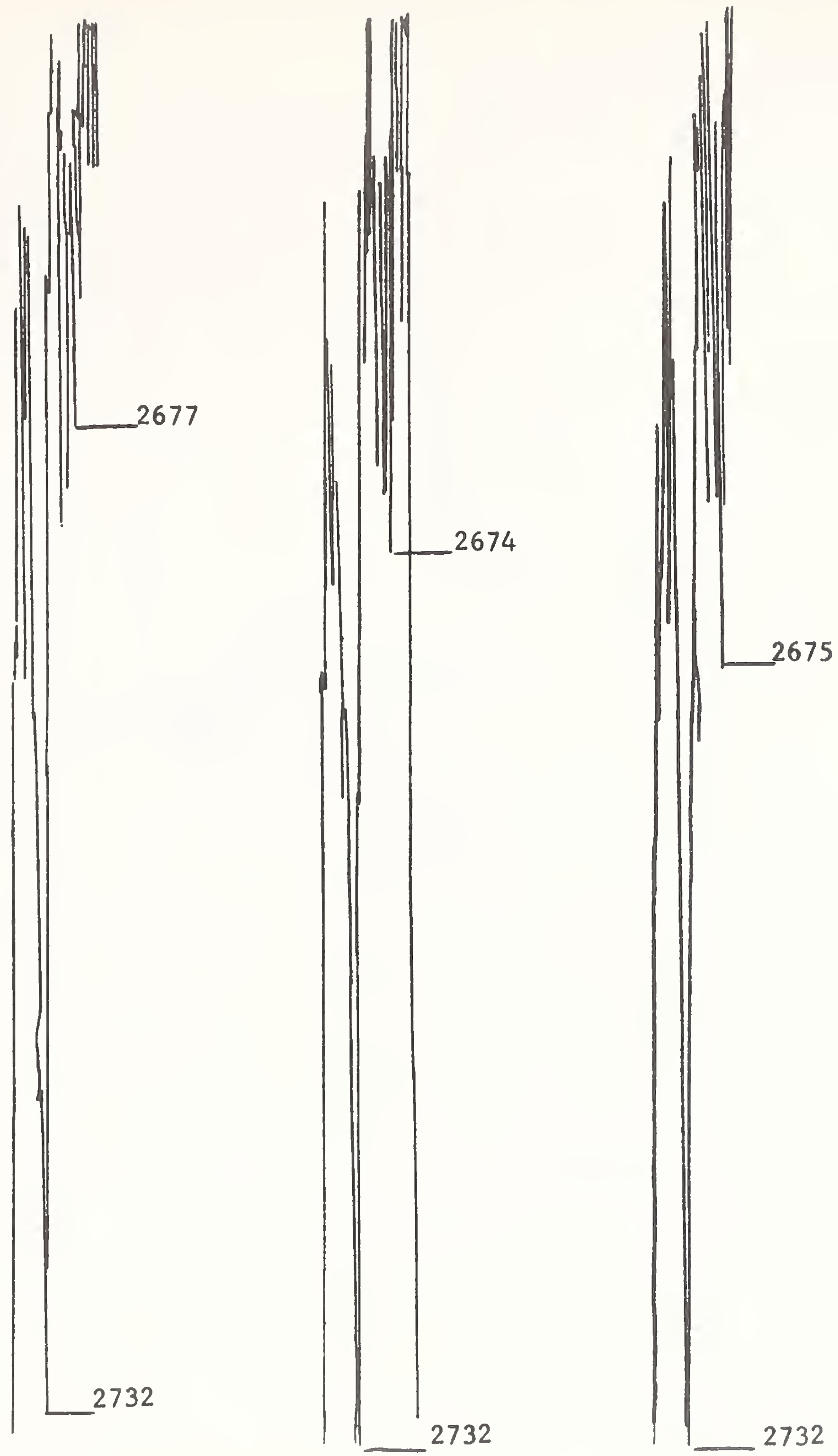


CH


WAVELENGTH IN MICRONS
FREQUENCY IN CM

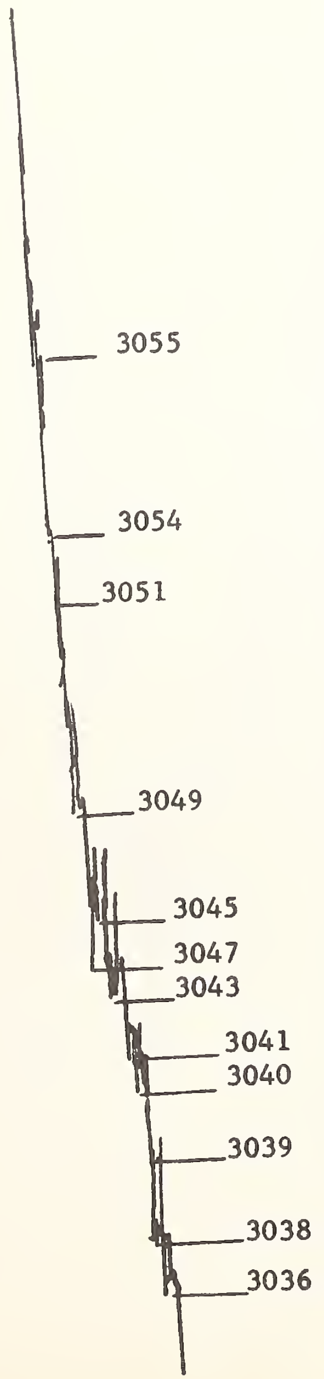


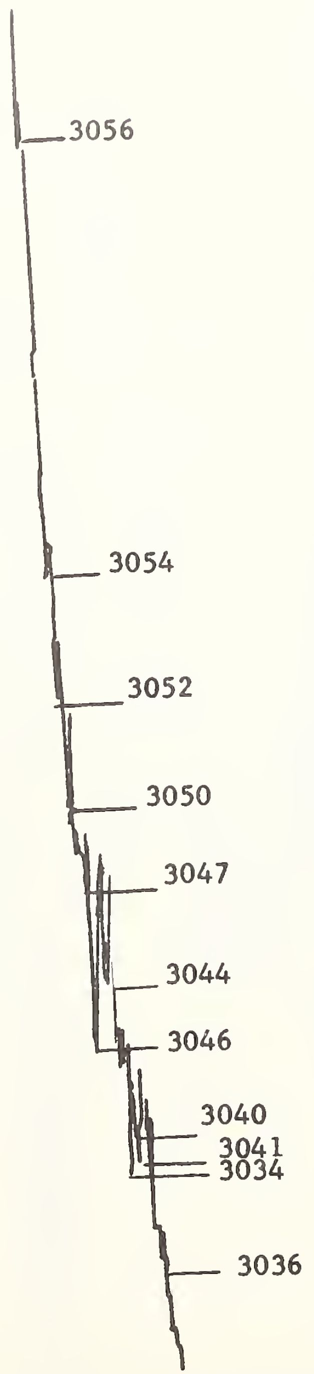
#12364 MC 8008
MC 800
CCl_4
Glower Current .6
Path .1 mm
Reference Air
Double Beam
Scale Selection X
Gain 100 x .669
Period 32
Scanning Speed 38cm $^{-1}$/min.
Chart Speed Standard
Scale Expansion 0-35 full
Date 2-3-64
Analyst - Lee

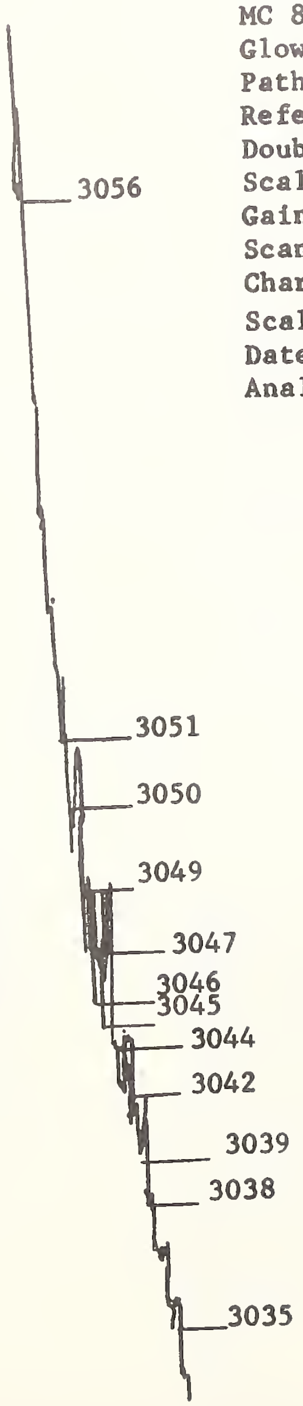


#12364 MC 8009
MC 800
CCl_4
Glower Current .6
Path .1 mm
Reference Air
Double Beam
Scale Selection X
Gain 100 x .669
Period 32
Scanning Speed 20 cm^{-1}/min.
Scale Expansion 20-40 full
Chart Speed Standard
Date 2-3-64
Analyst - Lee

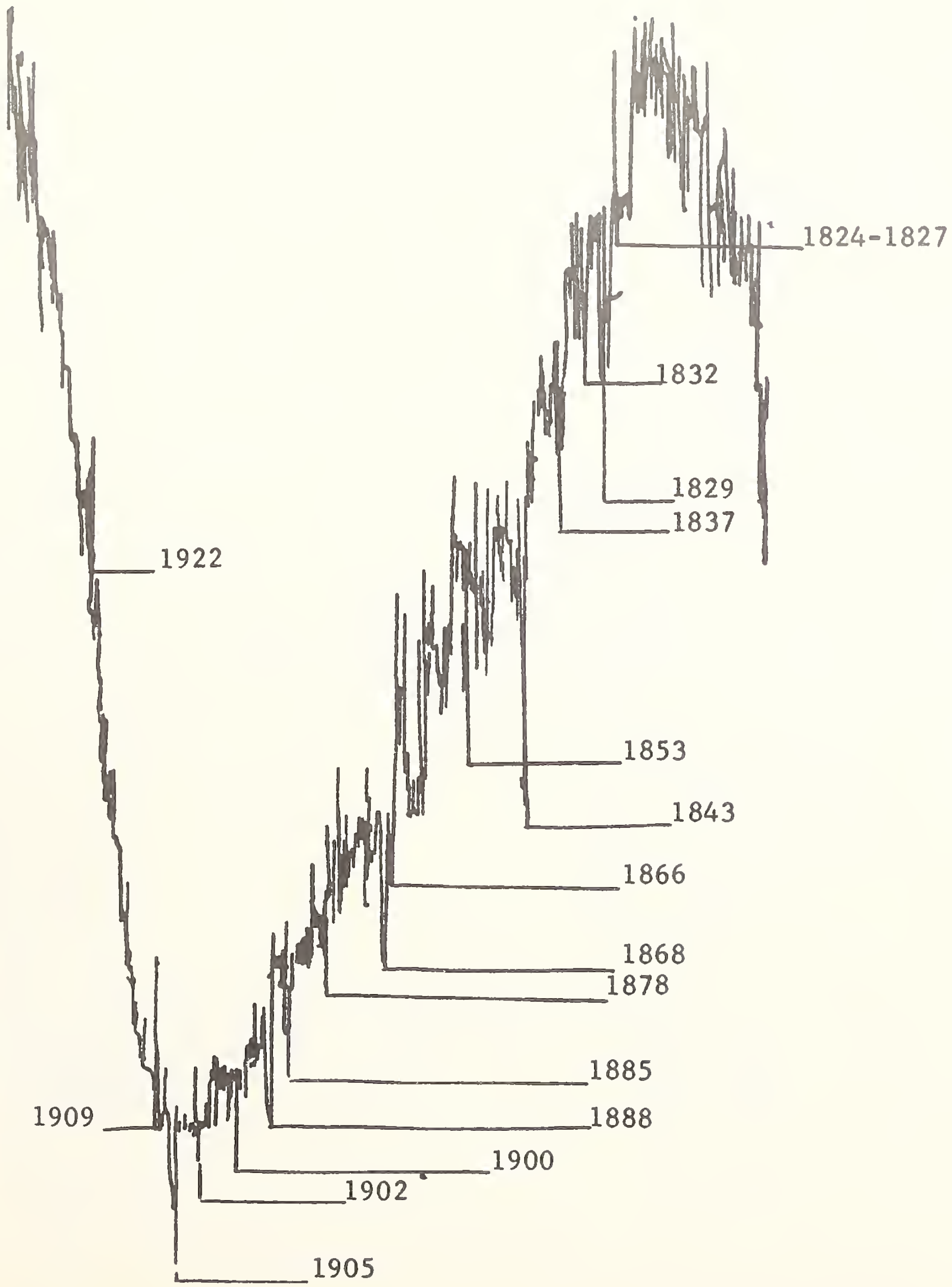
#12364 MC 800 10
MC 800
Glower Current .6
Path .1 mm
Reference Air
Double Beam
Scale Selection X
Gain 100 x .048
Scanning Speed 1.6 cm^{-1}/min.
Chart Speed 30 cm^{-1}/in.
Scale Expansion 10-15 full
Date 2-3-64
Analyst - Lee



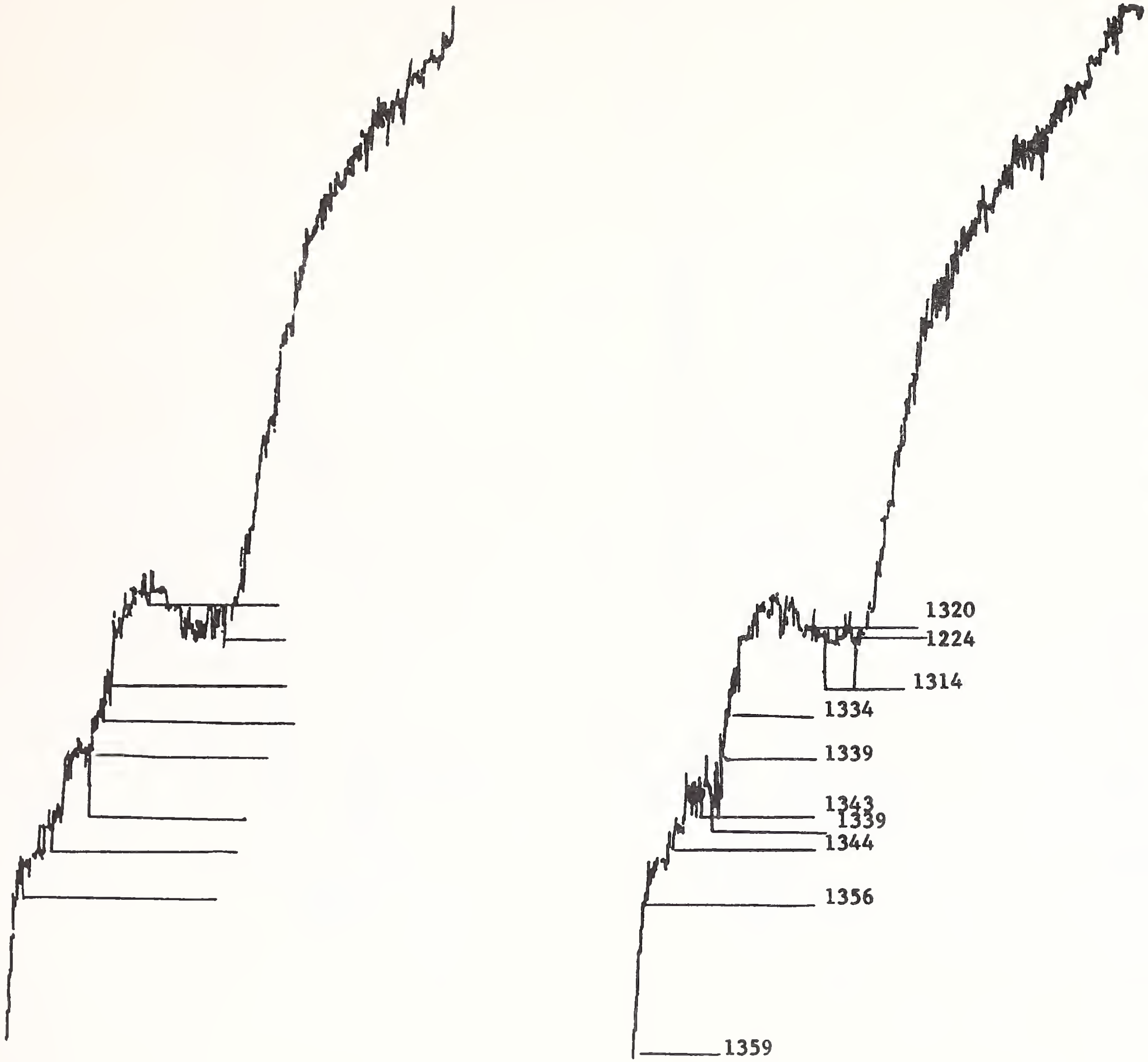




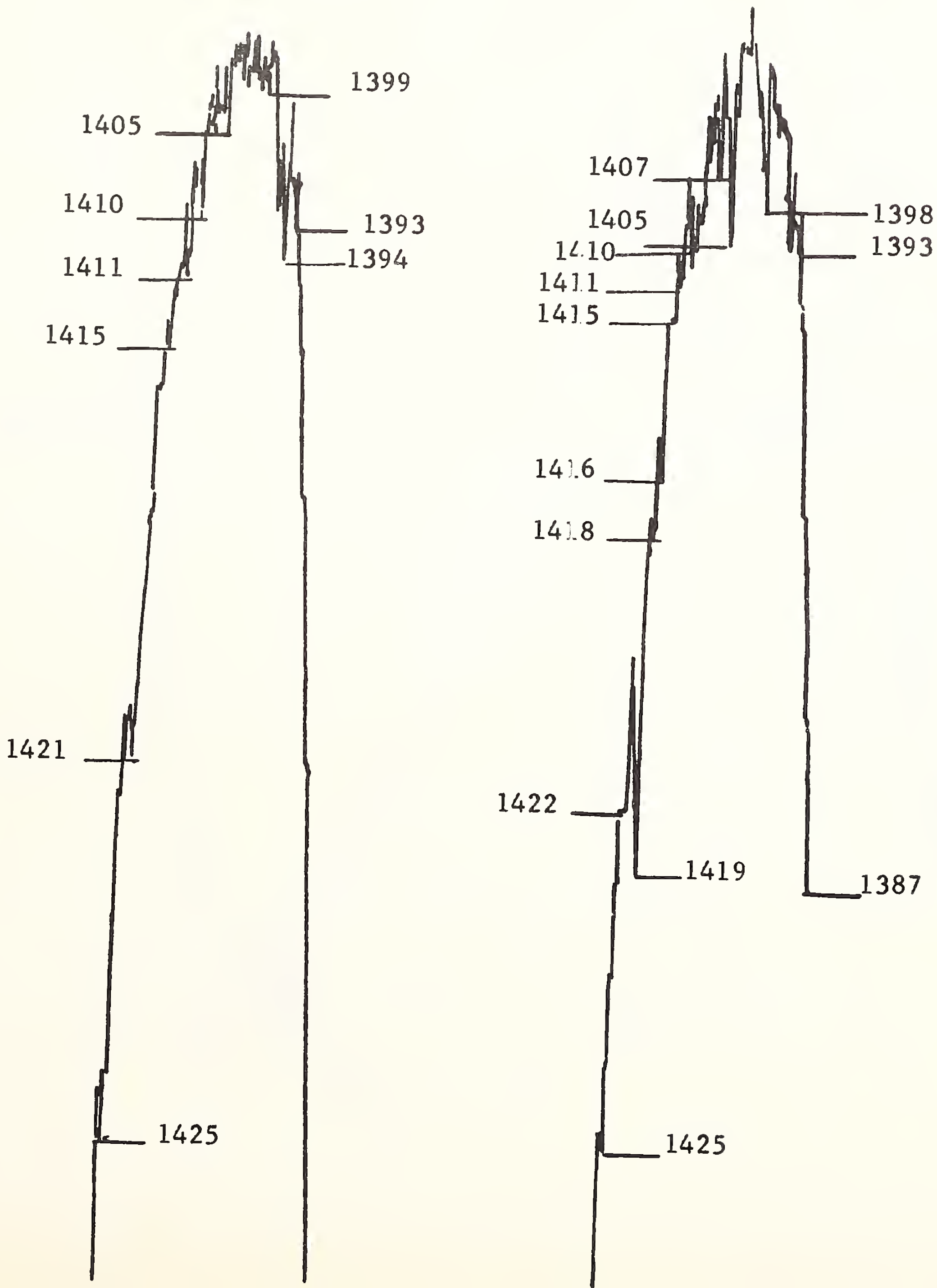
#12364 MC 80011
MC 800
Glower Current .6
Path .1 mm
Reference Air
Double Beam
Scale Selector X
Gain 100 x .048
Scanning Speed 1.6cm^{-1}/min.
Chart Speed 100cm^{-1}/in.
Scale Expansion 40-70 full
Date 2-4-64
Analyst - Lee



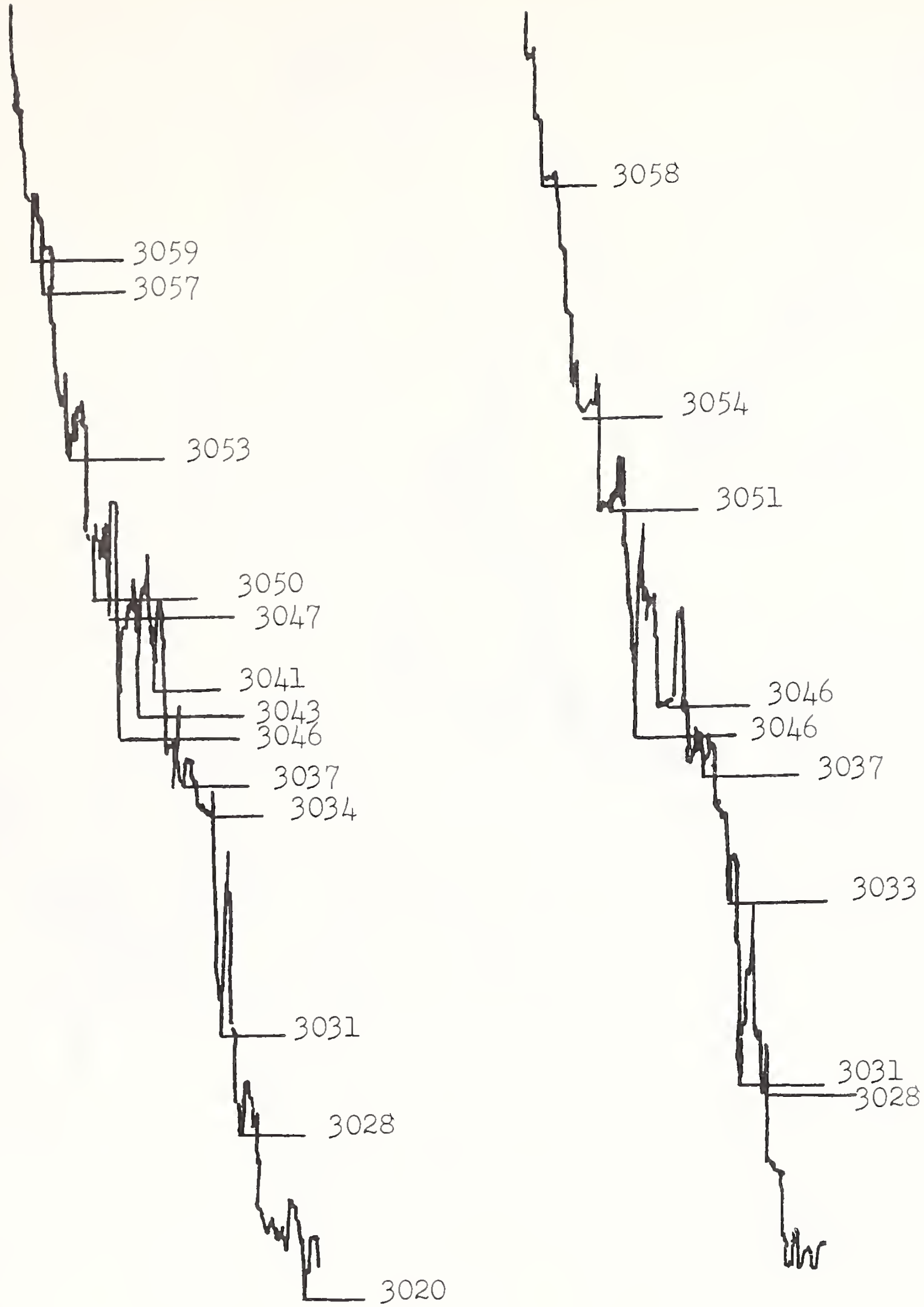
#12364 MC 80012
MC 800
Glower Current .6
Path .1 mm
Reference Air
Double Beam
Scale Selector X
Gain 100 x .048
Scanning Speed $3.2cm^{-1}/min.$
Chart Speed $100cm^{-1}/in.$
Period 8
Scale Expansion 60-80 full
Date 2-4-64
Analyst - Lee



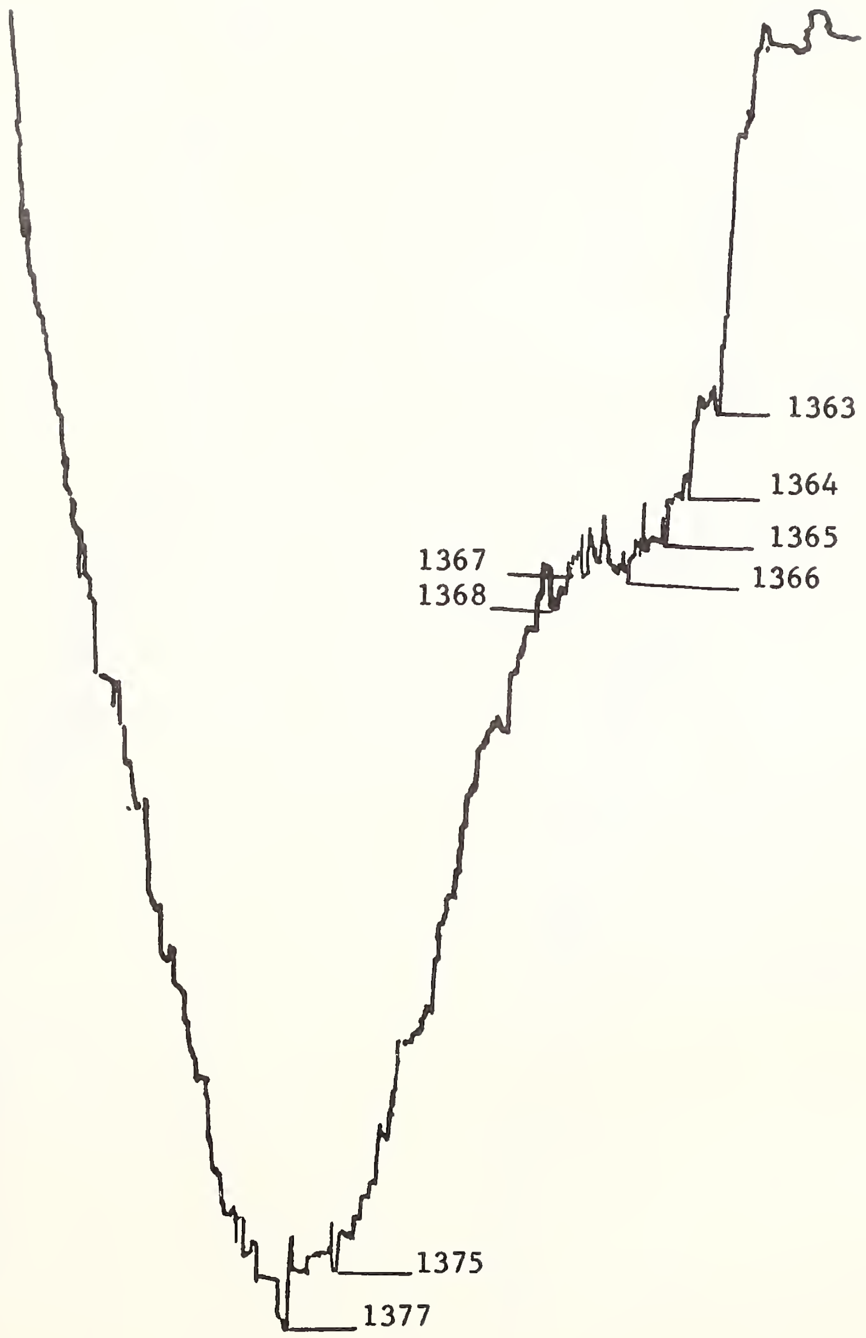
#12364 MC 80013
MC 800
Glower Current .6
Path .05 mm
Reference Air
Double Beam
Gain 100 x .044
Scanning Speed 3.2 cm^{-1}/min.
Chart Speed 100cm^{-1}/in.
Period 8
Scale Expansion 25-40 full
Scale Selection 2X
Date 2-4-64
Analyst - Lee



#12364 MC 800 14
MC 800
Glower Current .6
Path .05 mm
Reference Air
Double Beam
Gain 100 x .044
Scanning Speed 3.2 cm^{-1}/min.
Chart Speed 100 cm^{-1}/in.
Period 8
Scale Expansion 25-40 full
Scale Selection 2X
Date 2-4-64
Analyst - Lee

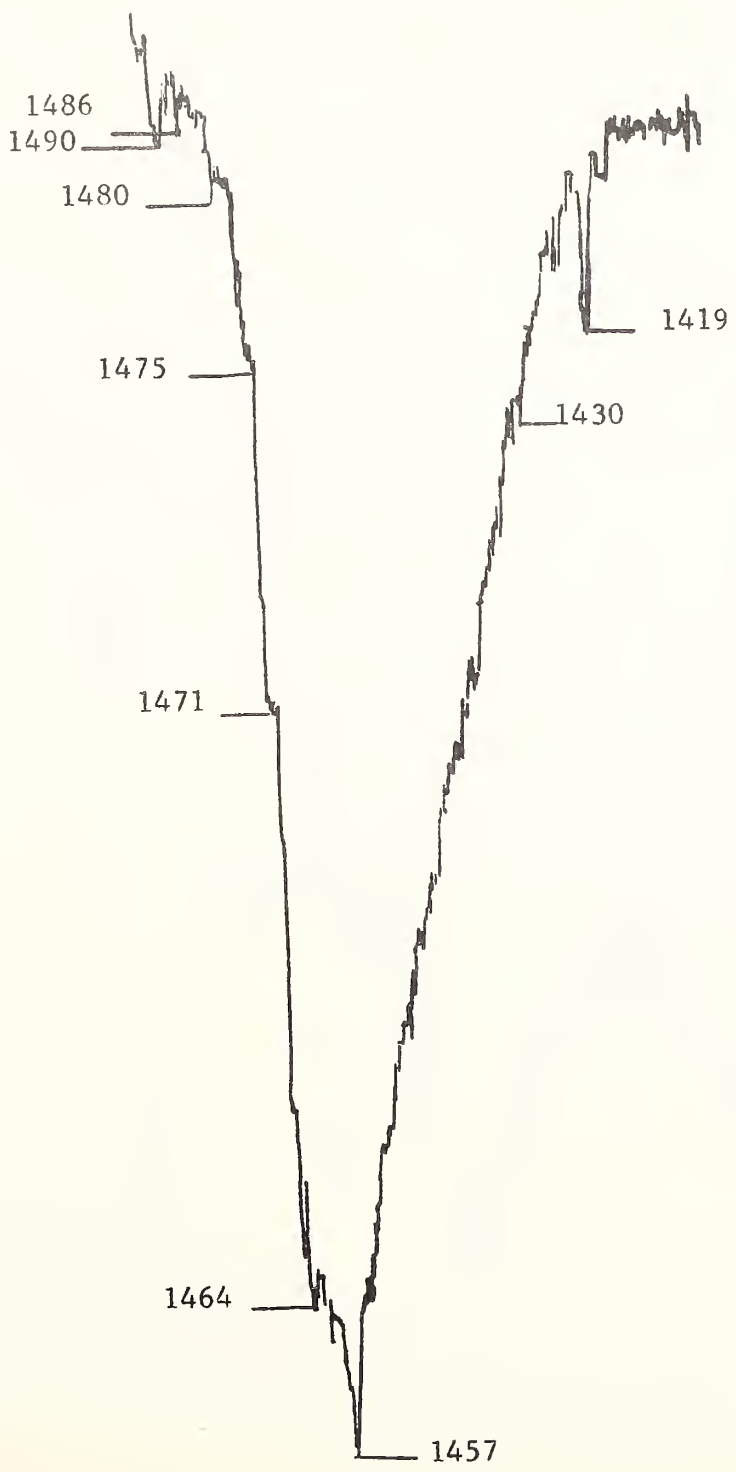


12364 MC800 15
MC 800
Glower Current, 6
Path .05 mm
Reference Air
Double Beam
Gain 100 x .044
Scanning Speed 1.6 cm^{-1}/min
Chart Speed 20 cm^{-1}/in
Period 8
Scale Expansion 25-40 full
Scale Selection 2X
Date 2-4-64
Analyst - Lee



#12364 MC 800 16
MC 800
Glower Current .6
Path .05 mm
Reference Air
Double Beam
Gain 100 x .044
Scanning Speed 1.6 cm^{-1}/min.
Chart Speed 20 cm^{-1}/in.
Period 8
Scale Expansion 5-25 full
Scale Selection 2X
Date 2-4-64
Analyst - Lee

#12364 MC 80017
MC 800
Glower Current .6
Path .05 mm
Reference Air
Double Beam
Gain 100 x .044
Scanning Speed 3.2 cm^{-1}/min.
Chart Speed 100 cm^{-1}/in.
Period 8
Scale Expansion 35-60 full
Scale Selection 2X
Date 2-4-64
Analyst - Lee



#12364800 MC 18
MC 800
Glower Current .6
Path Slide
Reference Air
Double Beam
Gain 100 x .044
Scanning Speed 3.2 cm^{-1}/min.
Chart Speed 25 cm^{-1}/in.
Period 8
Scale Expansion 25-50 full
Scale Selection 2X
Date 2-4-64
Analyst - Lee

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PART II AGGREGATE STUDIES

Introduction

The chemical nature of a mineral surface has prompted much speculation. People currently refer to mineral surfaces as acidic or basic although there is not good reason for doing so. The history of this designation stems from the time of the early prospector who carried hydrochloric acid in his field kit to help in the identification of certain minerals. Carbonates and sulfides were termed basic because they reacted with the acid. Silicates and quartzites on the other hand were acid since they did not react.

This classification scheme does not agree with the acid-base terminology used by the chemist except in special cases. For example sulfites will react with strong acids, yet in solution they are weakly acidic. There is nevertheless a marked difference in behavior between the so-called acidic and basic rocks with regard to acidic and basic asphalt emulsions so the acid-base terminology can be used as a means of contrasting behavior.

The project was designed with the idea of first developing a taxonomy whereby different minerals could be arranged according to adhesive ability with respect to suitably chosen standards and procedures. Although adhesion is easily defined in an intuitive way, it is not a property that can be directly quantified. Adsorption properties of solids however are measurable and as such, should correlate with adhesion.

The Nature of Solid Surfaces

Aggregates consist of great masses of crystals, randomly oriented and cemented by a matrix material composed of still smaller crystals. The size of the crystals and their internal defects such as vacancies, interstitials, and dislocations in the structure can have as great an effect on the properties of the system as the actual composition. As an example consider the members of the feldspar family ($KAlSi_3O_8$); sanidine, orthoclase, and microcline. While individual crystals which compose these may be of different size, the great difference in their properties is due to the regularity, or lack of it, with which the potassium and aluminum is found in the crystal lattice. Microcline has the most regular structure having cooled slowly, while sanidine is the most irregular. In addition, minerals having the same composition may exist in different crystal configurations. Sanidine and orthoclase have a monoclinic form while microcline slowly converts to a triclinic form by multiple body twinning. The inherent atomic geometry in all cases is tetrahederal.

From a purely chemical viewpoint, one would be tempted to conclude that all of these should show the same adhesion since they all have the same chemical composition. They must however, be regarded as "isomers" in a chemical sense as they have very different chemical properties. The surfaces of these materials will reflect in a real way, the differences in their internal structure.

The term adhesion represents the product of the number of chemical bonds formed between the aggregate and the asphalt multiplied by the energy per bond. A more irregular surface favors a greater number of bonds. A good measure of the irregularity of a surface is given by the surface area per gram of material. Under certain conditions it is possible to coat a surface

with a layer of gas or liquid one molecule thick. The material can then be desorbed from the surface and its quantity determined. The size of the molecules can be measured and the surface area can then be calculated. In practice, comparisons between different surfaces are of about equal value with the "absolute" measurements since there are always a number of uncertainties.

The energy per bond is dependent on the participants. Whenever a chemical bond is formed, electrons are re-distributed. It is this re-distribution that produces the bond energy. In this process, two electrons are usually involved because of an intrinsic property called spin. All substances with the exception of the inert gases have a tendency to either gain or loose electrons through re-distribution and bond formation. It is therefore possible to classify materials on the basis of this tendency.

<u>Lewis Acid Base Theory</u>

By definition, a Lewis acid is an acceptor of an electron pair and an electron donor is a Lewis base.

$$\underset{\text{Lewis Acid}}{H^+} \quad + \quad \underset{\text{Lewis Base}}{:O:H} \qquad\qquad H:O:H$$

Neutralization occurs, as in the example, with the combination of an electron acceptor with an electron donor.

An organic alcohol, such as ethyl alcohol, behaves as a base when in contact with an acid, donating a pair of electrons to achieve neutralization.

$$\underset{\text{Base}}{CH_3\overset{H}{\underset{H}{C}}:O:H} \quad + \quad \underset{\text{Acid}}{H:I} \longrightarrow \underset{\text{Base}}{H:O:H^-} \; + \; \underset{\text{Acid}}{CH_3\overset{H}{\underset{H}{C}}:I}$$

This same alcohol in a solution of a strong base will behave as an acid, acting as an electron acceptor.

$$\underset{\text{Acid}}{CH_3\overset{H}{\underset{H}{C}}:O:H} \quad + \quad \underset{\text{Base}}{Na:O:H} \longrightarrow \underset{\text{Acid}}{H:O:H} \quad + \quad \underset{\text{Base}}{CH_3\overset{H}{\underset{H}{C}}:O:Na}$$

This definition of an acid is an extension of the older one which defined it as something which yielded a proton in solution. The Lewis definition reduces to the older one whenever one of the reactants is water. Water is actually a weak base since it contributes an electron pair in the great majority of its chemical reactions. From the Lewis viewpoint, it is not possible, however, to classify any substance as acid or base since this depends entirely upon what it reacts with. Where specific mention is not made, water is always understood.

A complete transfer of electrons from base to acid is not required. The electrons participating in a chemical bond encircle all the atoms partaking of the bond. The charge density about the base is simply reduced by the formation of the bond, while the electron density about the acid is increased.

In the same manner, aggregates may behave as acids or bases. For example, in the case of emulsions we may have the following:

For quartzite:

$$\text{(1) Agg-O-}\underset{\text{O}}{\overset{\text{O}}{\text{Si}}}\text{-OH} \quad \xrightarrow{\text{in water}} \quad \text{Agg-O-}\underset{\text{O}}{\overset{\text{O}}{\text{Si}}}\text{-O} + H^{+}$$

$$\text{(2) Agg-O-}\underset{\text{O}}{\overset{\text{O}}{\text{Si}}}\text{-OH} \quad \xrightarrow{\text{in (Lewis) base}} \quad \text{Agg-O-}\underset{\text{O}}{\overset{\text{O}}{\text{Si}}}\text{-O} + H^{+}$$

$$\text{(3) Agg-O-}\underset{\text{O}}{\overset{\text{O}}{\text{Si}}}\text{-OH} \quad \xrightarrow{\text{in (Lewis) acid}} \quad \text{Agg-O-}\underset{\text{O}}{\overset{\text{O}}{\text{Si}^{+}}} + OH^{-}$$

Example (1), in a neutral media has an electronegative surface and would show maximum adhesion with a cationic asphalt or emulsion. Example (2), in a basic media has a greater tendency to donate a proton and is therefore more electronegative than (1) and would show even greater adhesion with a cationic asphalt or emulsion. Example (3) in an acid media has an electropositive surface and would show maximum adhesion with an anionic-type asphalt. The degree of electronegativity or electropositivity on the aggregate surface is dependent upon the ease of ionization of the surface in conjunction with the relative

Lewis basicity or acidity of the medium surrounding the surface.

For a limestone or basic type aggregate sample:

(1) Agg-Ca-CO_3H $\xrightarrow{\text{in water}}$ Agg-Ca^+ + HCO_3^-

or

Agg-Ca-OH $\xrightarrow{\text{in water}}$ Agg-Ca^+ + OH^-

(2) Agg-Ca-CO_3H $\xrightarrow{\text{in base}}$ Agg-Ca-OH (Exchange)

in base Agg-Ca-CO_3 + H^+

The charge separation brought about by the ionization can persist to only a small degree since large electric fields are created at the surface. These fields in turn must be neutralized by the breaking up of the emulsion with consequent coating of the surface. The surface interactions in the coated state cannot involve ionic forms in the case of asphalt since the dielectric constant is much too small to permit the formation of the necessary double layer. Also interactions of this type are not sufficiently strong to tightly bind the asphalt to the rock.

It should be possible to assign a Lewis acid or base character to a mineral surface. This would be a parameter telling how well the surface liked or disliked electrons. A convenient measure of this would be the activation energy for adsorption for known Lewis acids and bases. The activation energy represents the energy needed by a particular atom or molecule to escape from the surface. The surface could also be brought to equilibrium in the presence of two or more Lewis acids of differing strength. The fractional part of the surface covered by each indicates a measure of its strength as a base.

Adsorption Studies

A program was initiated to study the adsorption characteristics of aggregate samples in aqueous solutions. It was expected that this would yield quantitative information as to the relative surface area and surface inter-

actions prevalent with a given type of aggregate. This information should be of immediate use in determining the effects of adhesives on surfaces. Stripping involves a competition between water and asphalt for bonding positions on the aggregate surface. Studies with aqueous solutions should then reflect competitions between water and whatever is dissolved in it. Since a polarograph was available, a procedure based on this instrument was attempted.

1. Theory of Adsorption

At any boundary surface separating media of differing dielectric constants there exist short range electric fields. These fields are often referred to as Van der Waal forces. If the kinetic (thermal) energy of a particle is less than the potential energy associated with this force, then the particle is bound on or very near the surface and is said to be adsorbed. The amount of material that a given surface will collect is dependent on the surface area and on the specific electrical nature of the surface and material. A continual interchange occurs between material on the surface and "free" material. After a short period of time an equilibrium is established, at which time the rate of material leaving the surface is the same as that returning. A particle will leave the surface as soon as it has acquired enough energy to overcome the potential energy barrier. Statistical mechanics tell us that the fractional number of particles having an energy greater than any energy E is given by $\exp{-E/kt}$, where k is the Boltzman constant and t is the absolute temperature. The rate of particles returning to the surface is dependent on their concentration near the surface, and possibly the fractional part of the surface that is unoccupied. Assuming a simple proportionality for the rates:

$$\text{Log } C = \text{Log } N - E/kt$$

C is the concentration of adsorbed material; N is a proportionality constant, and E is now the energy of the surface barrier called an activation energy. If the logarithm of the concentration is plotted against 1/t, a straight line

results, the slope of which gives the activation energy for the surface. This energy can be interpreted as the bond energy between the surface and the adsorbed material. If it is greater than about 10 Kcal/mole the exchange rate between surface and media is very slow at room temperature, and a definite chemical bond is said to exist. The term chemisorption is often used to describe this type of adsorption. In time, adsorbed material may penetrate into the bulk of the adsorbent.

If the energy is less than 10 Kcal/mole the process is classified as physical adsorption, and this usually results in the formation of a layer of adsorbed material one molecule thick. The process is fast and there is no appreciable penetration of the adsorbed material into the bulk of the adsorbent. Adsorption studies of this type are often carried out in the gas phase in order to determine surface areas for catalysts.

(B.E.T. Method)

This method of study should yield very interesting results but was not within the scope of the current project. The measurements are usually conducted in the 60-80 K° range so a supply of liquid nitrogen and associated cryogenic equipment is required.

The adsorption process is usually somewhat more involved than indicated in the previous paragraph. Equilibria exists in solution between the surface and all the ions or molecules present. Different particles compete for positions on the adsorbent, those with higher activation energies displacing lower ones and being preferentially adsorbed. Dislocations and holes in the solid lattice allow penetration of particles into the surface and may lead to unexpected adsorptions of material of just the right size to fit into the holes. For example potassium containing minerals will hold large amounts of argon since the argon atom is the same size as the potassium atom and will fit into its positions in the crystal. Regions of high electric field called surface

active sites often exist. Particles are adsorbed at these sites and then migrate along the surface in all directions. Correction terms must be included in the calculations for these effects. The term "particle" is used to embrace atoms, molecules, free radicals and positive or negative ions. Neutral particles are attracted to the boundary since the electric fields (van der Wall forces) associated with the atoms of the adsorbent are very inhomogeneous near the boundary. These fields distort the charge distribution in the neutral material producing a positive and negative side. The polarized material is then attracted to the boundary. When contact is made, charges are more permanently redistributed and a weak chemical bond is formed. The ability of a particle to become polarized, or to acquire an induced dipole moment is termed its polarizability. In general, the greater the polarizability, the larger the extent of adsorption and the greater the activation energy. The electronic clouds associated with Lewis bases are easily polarized. Certain Lewis acids such as metal ions are also easily polarized, so there is no absolute relation between the polarization and acid-base strength.

In the case of charged particles such as ions, what is called a double layer is formed. The charged particles cover the surface, and directly above, ions of opposite charge are found so that the surface appears uncharged when viewed from a distance. The dielectric constant of the surrounding media is important since the force of attraction between the separated charges of the double layer varies in inverse proportion to it. A small dielectric constant (3 for asphalt) means that forces tending to collapse the double layer are large; larger than the polarization forces which hold the ions to the surface. Hence only a small double layer can be formed and we can have adsorption of neutral material only. In the case of water, the dielectric constant is 81 and the recombining forces are small. A large double layer can exist. Both positive and negative ions as well as neutral atoms can exist on the surface

at the same time with a small double layer being formed to neutralize excess surface charge.

In solution, adsorption usually follows the Freundlich equation:

$$\log C = n\log x + n\log km$$

x is the mass of substance adsorbed; m is the mass of the adsorbent; C is the concentration of the solution at equilibrium; k and n are empirical constants.

The equilibrium concentration in the formula can be replaced by the initial concentration over certain ranges without destroying the linear feature of the equation. This has been done in evaluating the data since it facilitates comparison of different samples. This is permitted mathematically since the equation is empirical.

2. Laboratory Procedure

Copper was first chosen since its ions are easily polarized. It will form complexes with many substances and can be expected to have a high adsorption activation energy. Previous work at the Materials Laboratory by Mr. R. H. Gagle established that washing aggregate with metal salts promoted asphalt adhesion. Copper sulfate solutions of known concentrations were prepared and run on the polarograph. Miscellaneous samples of aggregate, varying in size and composition, were placed in known amounts of the copper standards and allowed to stand overnight. Portions of the solutions were removed and the concentrations compared with the original standards. All showed appreciable adsorption. Runs were made to determine temperature dependence. No attempt was made to calculate activation energies since the temperature control was poor during the experiment, but the adsorption was definitely temperature dependent as predicted. It was decided at this point to concentrate efforts on samples of simple and known composition such as Ottawa sand, feldspar, etc., before proceeding to more complicated aggre-

gates. This would allow their use as comparative standards to rate the more complicated aggregates.

The analysis of the solutions was carried out with the aid of a Sargent polarograph according to the procedures contained in Linganes' Electroanalytical Chemistry. A great deal of difficulty was encountered with copper due to a disproportionation reaction which occurs and in an effort to obtain better data, zinc solutions were utilized and the same procedure followed.

The polarograph is not a good instrument for such experiments as only a small decrease in relatively concentrated solutions is observed and the charts are difficult to read to the required degree of accuracy. It offers a potential advantage however, in that the competition between a number of positive ionic species could be followed. Superior data undoubtedly could be obtained by means of a bridge arrangement and two rotating platinum electrodes rather than by use of the dropping mercury electrode.

The data is given in Tables II to VII. The values for the diffusion currents are in microamperes.

Plate 1 shows a typical chart as obtained from the polarograph. Tangent lines are drawn parallel to one another at the points on the top and bottom of the curve where the curvature changes sign. The turning point at the bottom is especially hard to locate at times. There is a small damped oscillation imposed on the more rapidly varying diffusion current, so there are several turning points at the bottom. The one nearest the main portion of the curve must be used. If this procedure is not followed, the diffusion currents will not be reproducible or linear with respect to concentration. It was possible to duplicate successive runs to within one scale division. No special attention was paid to temperature control although this was constant to within two degrees C.

Plate 2 shows a plot of diffusion current versus concentration. It was necessary to re-run the standards at the same time as the unknowns as the instrument characteristics were not constant over extended periods of time.

Aggregate Ion Adsorption

Adsorption of zinc ions on aggregate surfaces is illustrated in Plate 3 for various concentrations on $ZnSO_4$ solution. The quantity of zinc ions adsorbed is related to the concentration of ions initially present and the quality of the aggregate when aggregate surface area (by mesh size), aggregate mass, and temperature are maintained constant. Polarographically, the ion concentration is interpreted as diffusion current and thus changes in concentration are determined by changes in diffusion current.

The petrographic analysis for the mineral samples is given in Part III along with results of a strip test.

3. Experimental Data

Decomposed Granite

Samples of decomposed granite of different mesh size were prepared by screening. One gram samples were deposited together with 50 ml. of $ZnSO_4$ solutions of .001 M; .003 M; .005 M; .007 M concentrations in small flasks and allowed to stand for periods in excess of 48 hours. 5 ml portions of the solutions were mixed with 15 mls of 1.0 N KCl and run on the polarograph along with samples of the initial standards. The temperature was kept constant within about 2 degrees during the runs. The quantity of zinc sulfate adsorbed was then calculated and plotted. Three charts were recorded on the polarograph and the average of these was used.

The isotherms are shown in Plate 4. All of the runs gave isotherms of the same slope, but different mesh sizes yielded different intercepts. The 60-80 mesh run yielded adsorption independent of concentration, and the

PLATE I
POLAROGRAPHIC CURVE

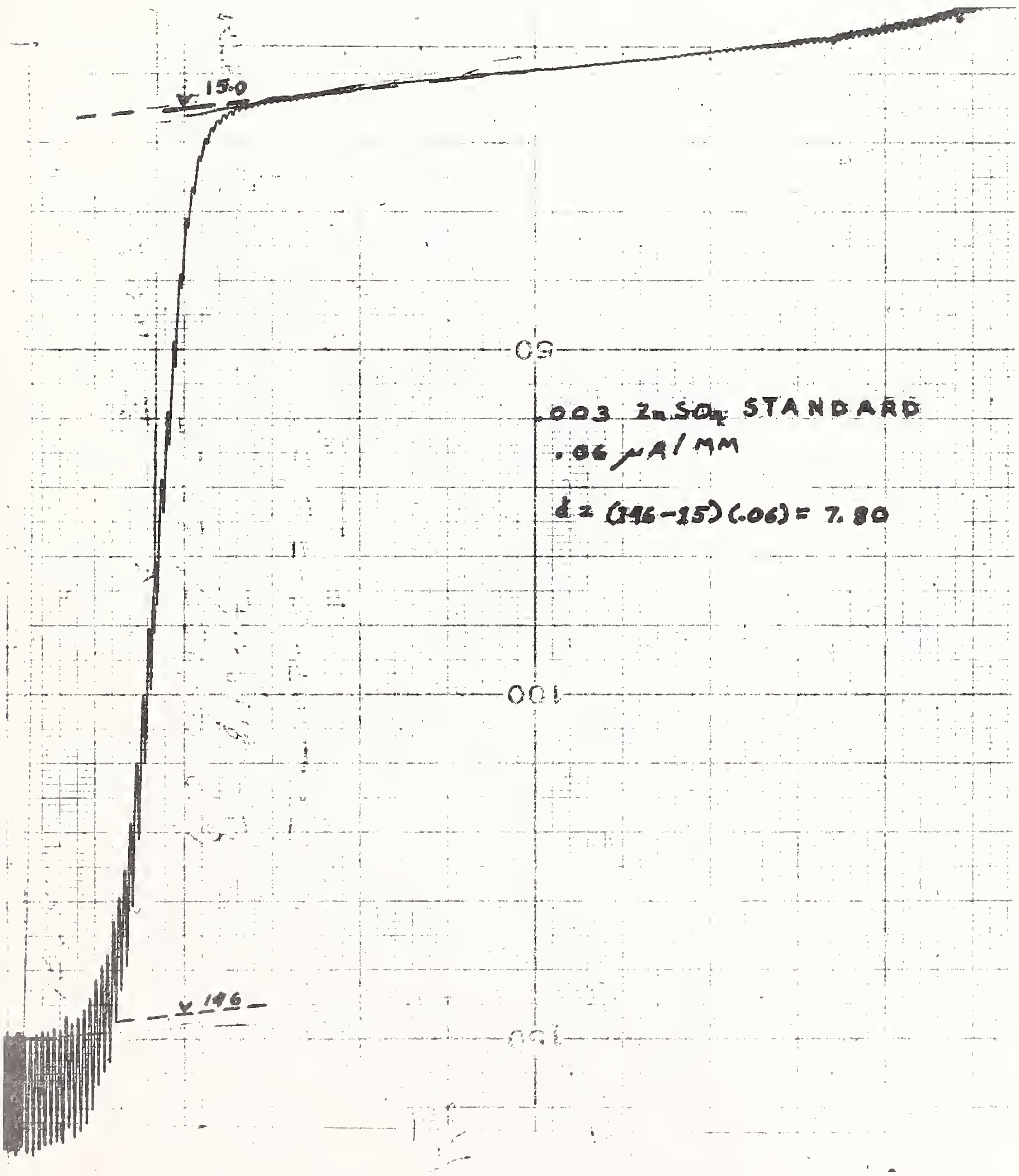
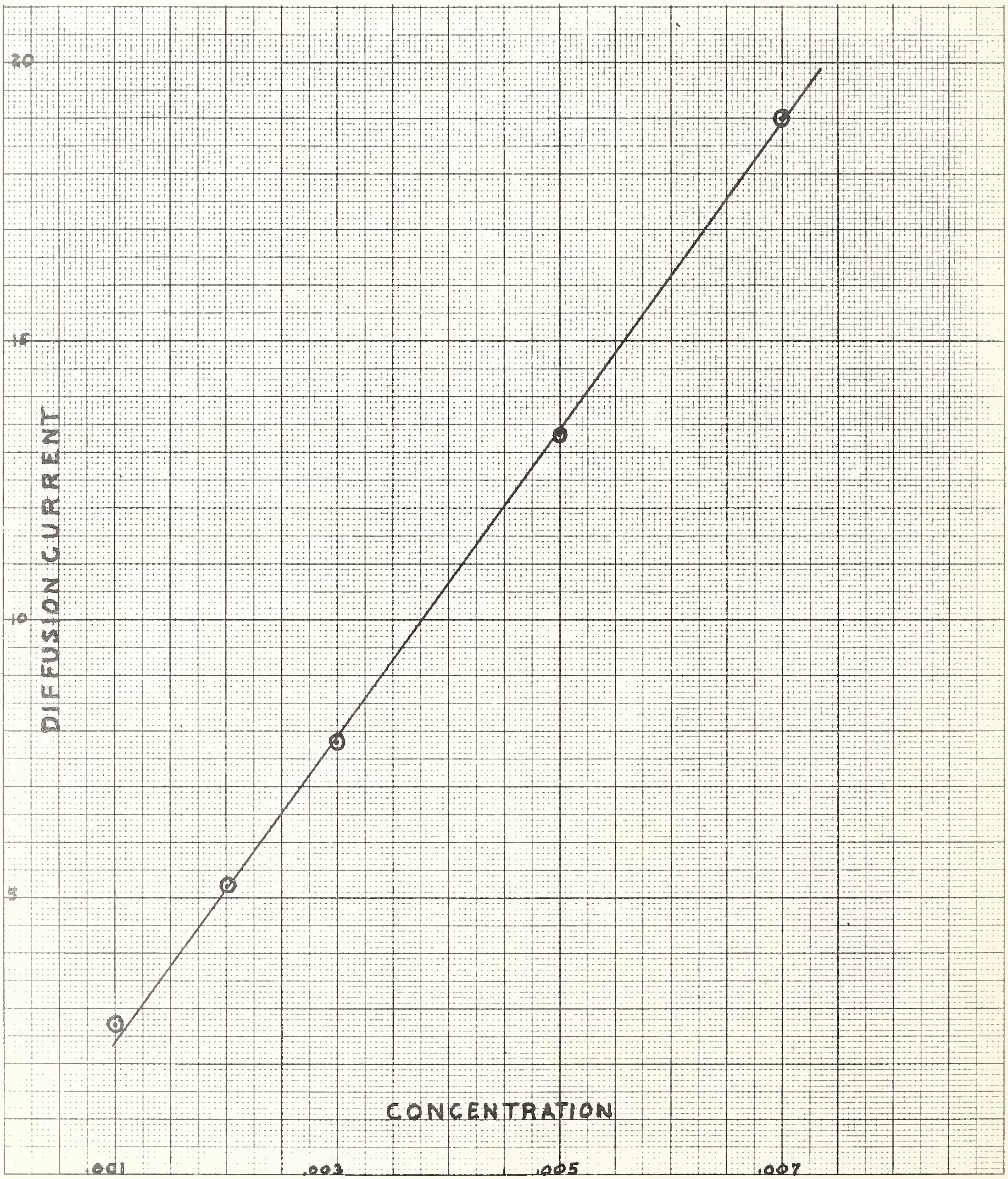


PLATE 2



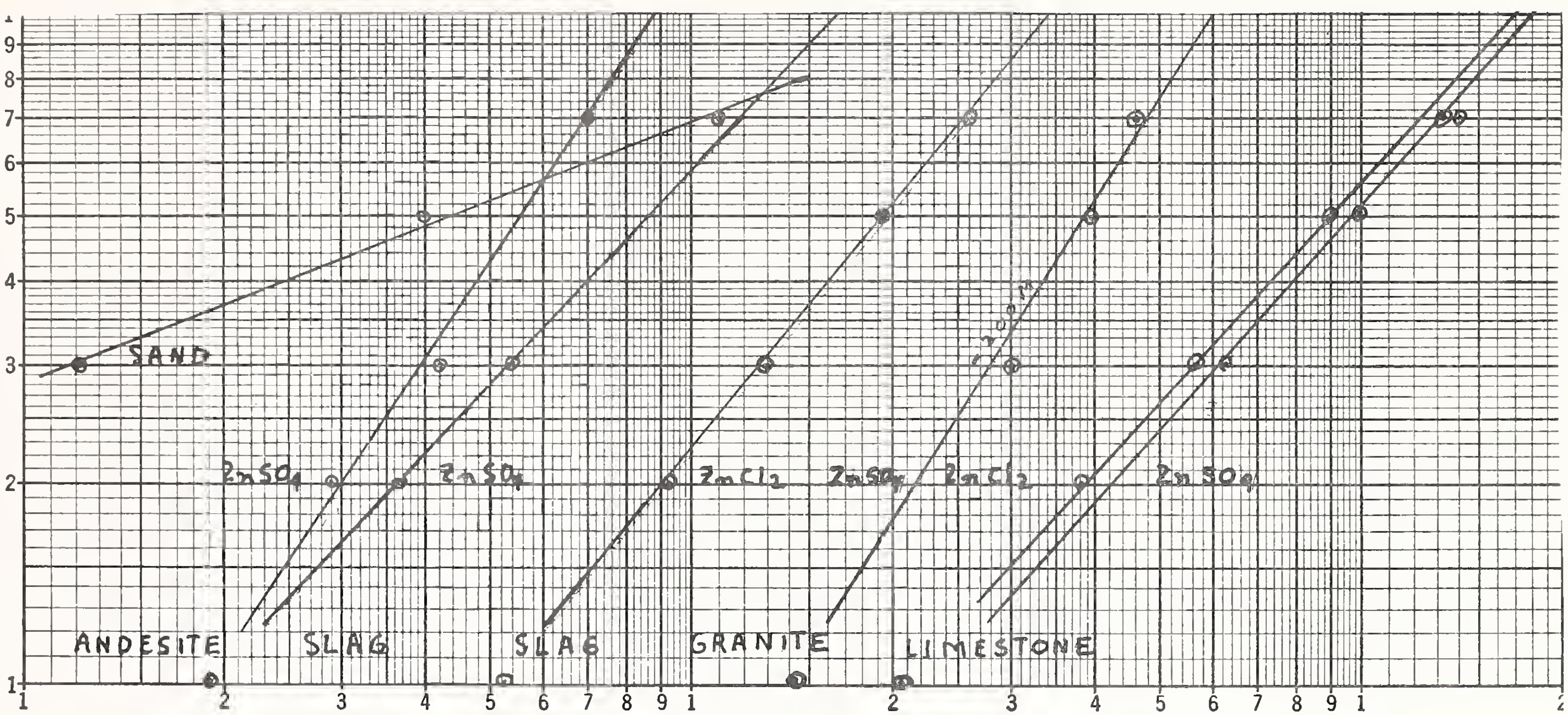
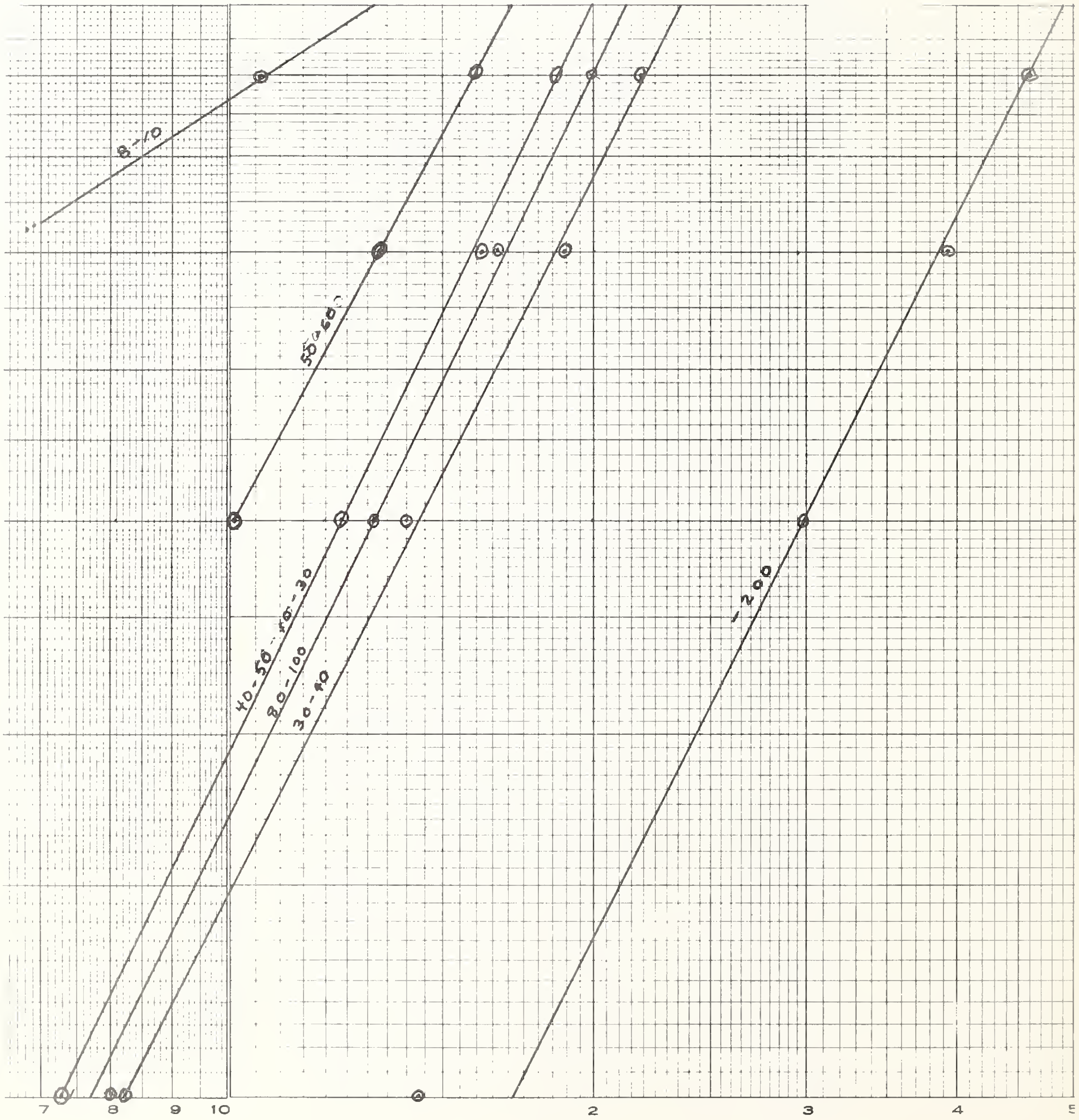


PLATE 3

ADSORPTION VS CONCENTRATION

PLATE 4
ADSORPTION ISOTHERMS
DECOMPOSED GRANITE



100-200 mesh run was inaccurate due to machine noise. The particle gradation of the granite is given in Table I.

In all cases the change in diffusion current has been plotted as equivalent to quantity adsorbed. This is valid because of the linear relation established by Plate 2. The intercepts of the graphs will include this proportionality factor which does not alter relative values.

TABLE I SAMPLE GRADATION

DECOMPOSED GRANITE

Mesh Size	+8	8-10	10-30	30-40	40-50
% of Total	6.1588	3.2282	34.0821	6.7539	13.9988
Mesh Size	50-60	60-80	80-100	100-200	200
% of Total	7.3638	7.7655	4.7604	9.6994	6.1886

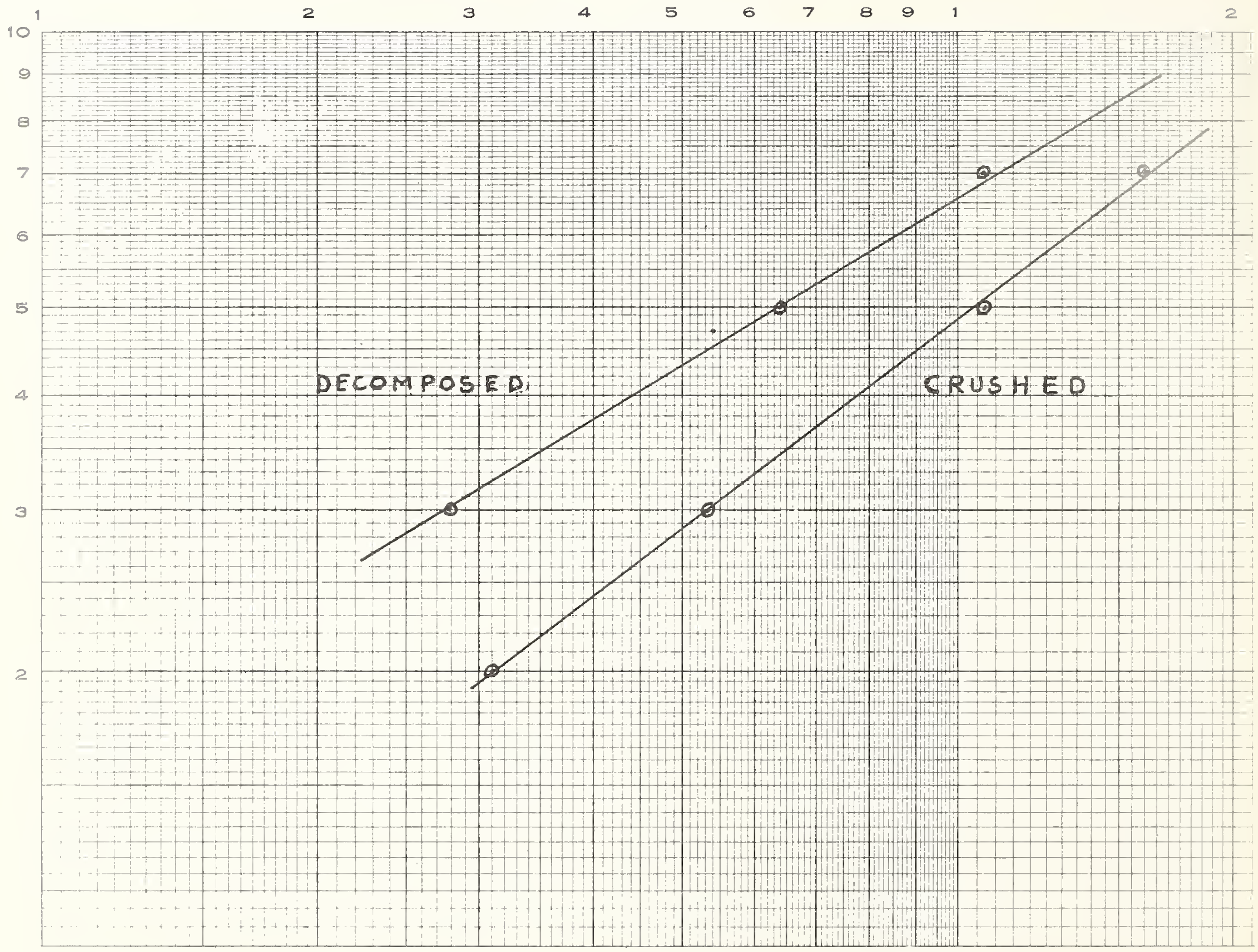
OTTAWA SAND

Mesh Size	+8	8-10	10-30	30-40	40-50
% of Total	-	-	-	819	22.72
Mesh Size	50-60	60-80	80-100	100-200	200
% of Total	16.019	23.810	12.820	22.640	1.1569

Crushed Granite

A sample of hard granite from the same outcropping as the decomposed granite was crushed and the 8-10 mesh portion was separated and run in the prescribed procedure. The crushed granite shows a higher adsorption than the decomposed material. Of greater significance is the behavior of the slopes and intercepts of the two samples as shown in Plate 5. The smaller

PLATE 5
ADSORPTION ISOTHERMS



intercept for the decomposed material is indicative of the much smaller surface area. Weathering would be expected to increase surface area and so does not account for this.

The decomposed material probably contains a great deal more adsorbed material due to weathering. There is some indication that atmospheric oxygen is adsorbed by many mineral surfaces including the granite. Supporting data for this will be given later.

Ottawa Sand

Sample of Ottawa sand were prepared in the same manner and run. A definite adsorption occurred in all cases but the amount is too small to be accurately measured by the difference method with the polarograph. The adsorption seems to be about a tenth that of the granite. Mesh size has a definite effect, the finer material having greater adsorption. A scatter plot was made on log-log paper and median points fell along a line which indicates the Freundlich equation is also obeyed by the sand. This particular graph is not included as only very rough methods were used to obtain the median points.

Andesite

Plate 3 shows adsorption for andesite.

Limestone

A sample whose petrographic analysis was 90% limestone and 10% quartzite was checked for adsorption with both zinc sulfate and zinc chloride solutions using the same procedure. A 4-10 mesh range sample was used. The isotherms are shown in Plate 3.

Basic Slag

Plate 3 shows adsorption for a basic slag. Of significance is the reversal of the position of the chloride and sulfate curves as compared with the limestone (Plate 3). The material presents a higher effective surface area to the chloride than to the sulfate.

Adsorbed Oxygen

Various mineral samples were brought to equilibrium in water, KCl was added as a supporting electrolyte, and in certain cases gelatin was added to supress maxima in the curves. The resulting solutions were scanned polarographically to determine any ionization. The resulting half-wave potentials and diffusions currents were recorded for all peaks observed and are given in Table VIII. Oxygen peaks were consistently observed with a number of minerals in spite of stringent efforts to outgas the solutions prior to mixing by means of a nitrogen purge. The fact that all samples do not show the oxygen peak leads to the belief that certain of the minerals notably the silicates have a layer of adsorbed atmospheric oxygen.

The reactions observed are:

1st wave	$O_2 + 2\ H^+ + 2e$	H_2O_2	-0.05 V
2nd wave	$H_2O_2 + 2\ H^+ + 2e$	$2H_2O$	-0.94 V

A half-wave potential of approximately -0.9 V with respect to a standard calomel electrode was observed with many of the aggregates which show poor adhesion. The fact that certain stockpiles decrease in adhesive ability with age may be explained by assuming that surface fractures are acquiring an adsorbed layer of atmospheric oxygen which prevents adhesion with asphalt. No attempt has been made to verify this by other means however.

Other potentials corresponded roughly to metals expected to be in the mineral. No significance was attached to the magnitude of the diffusion current.

4. General Conclusions

Plate 3 suggests the possibility of classifying surfaces as to Lewis acids or bases according to adsorption. Consider the basic slag. The chloride adsorption curve is to the right of the sulfate indicating a

TABLE VIII

SAMPLE	ADHESION	CONSTITUENTS	$E_{\frac{1}{2}}$	d(ua)
227257 Quartzite	10%	SiO_2	-0.962	.342
227516 Granite	25%	SiO_2;Ca;Mg;Al Fe	-0.94	.336
			-0.98	.56
228305 Sandstone Feldspar	25%	SiO_2;K;Al	-0.880	.204
			-0.946	.430
			-0.920	.450
			-1.653	5.2
			-1.60	6.9
			-2.463	22.0
			-2.433	46.8
222392 Andesite	15%	SiO_2;Mg;Ca;Fe	-1.594	5.2
			-1.686	13.6
			-1.643	12.0
			-1.620	5.8
			-1.624	10.8
			-2.460	54.6
227840 Basic Slag	90%		-.450	2.08
			-1.02	.424
			-.9455	.180
221684 Complex agg.	30%		-.910	.480
			-.925	.420
			-.946	.306
240089	65%	SiO_2;Al_2O_3	-1.02	.384
			.96	.380
			.975	.360
226542 Limestone	40%		NO PEAKS FOUND	

greater effective surface area for the chloride than for the sulfate. Both the chloride and sulfate ions are Lewis Bases since they can contribute a pair of electrons. The surface must act as a Lewis acid with respect to these. The more acidic the surface, the greater the spread between the curves.

We can look at this from a slightly different viewpoint. If the surface were infinitely basic, or had zero acidity, it would be covered entirely with zinc and the nature of the anions would have no effect on the adsorption curve. A less basic or slightly acidic surface would be partially covered with zinc and partially covered by the anion. Changing the anion results in an increase or decrease of the zinc on the surface, and a shift in the isotherm. A shift in the isotherms is reflective of change in that portion of the surface not covered by the zinc. In the case of the basic slag this is large, indicating a relatively large amount of anion on the surface, or that the surface is acidic when compared with the limestone.

If the basisity of the surface is greater than the basisity of the anions, then the least basic or more acidic will be preferentially adsorbed and will appear on the right. If the basisity of the surface is less than the basisity of the anions, then the more basic or least acidic will be preferentially adsorbed and will appear on the right.

It was the intention to obtain families of curves of this type using many different anions and cations. The relative acidity or basisity of a surface could then be determined by the crossover points in the curves. It is interesting to note that the adhesion for the basic slag is 95% while that of the limestone is 40%. We attribute a more acidic character to the basic slag and this correlates with the fact that adhesive agents are all basic in character.

The correctness of the classification of these surfaces could be cross-checked experimentally by doing adsorption runs in which the cation (zinc) is changed while the anions are left common. One would expect the limestone to change while the slag was unaltered.

Surface Area

The relation between the intercepts of the isotherm curves and the surface area is not immediately obvious but the fact that surface area is extensive, that is doubling sample size doubles surface area, implies that the intercept is proportional to the percent of surface area covered. Thus, relative surface areas can be obtained. The proportionality constant could be related through ionic radii to absolute surface area but the labor does not seem justified.

The relation between mesh size and surface area seems to be quite strange. The relative adsorption was plotted against average mesh size and is shown in Plate 6 for the granite. A similar curve is obtained by plotting maximum adsorption values for the Ottawa Sand.

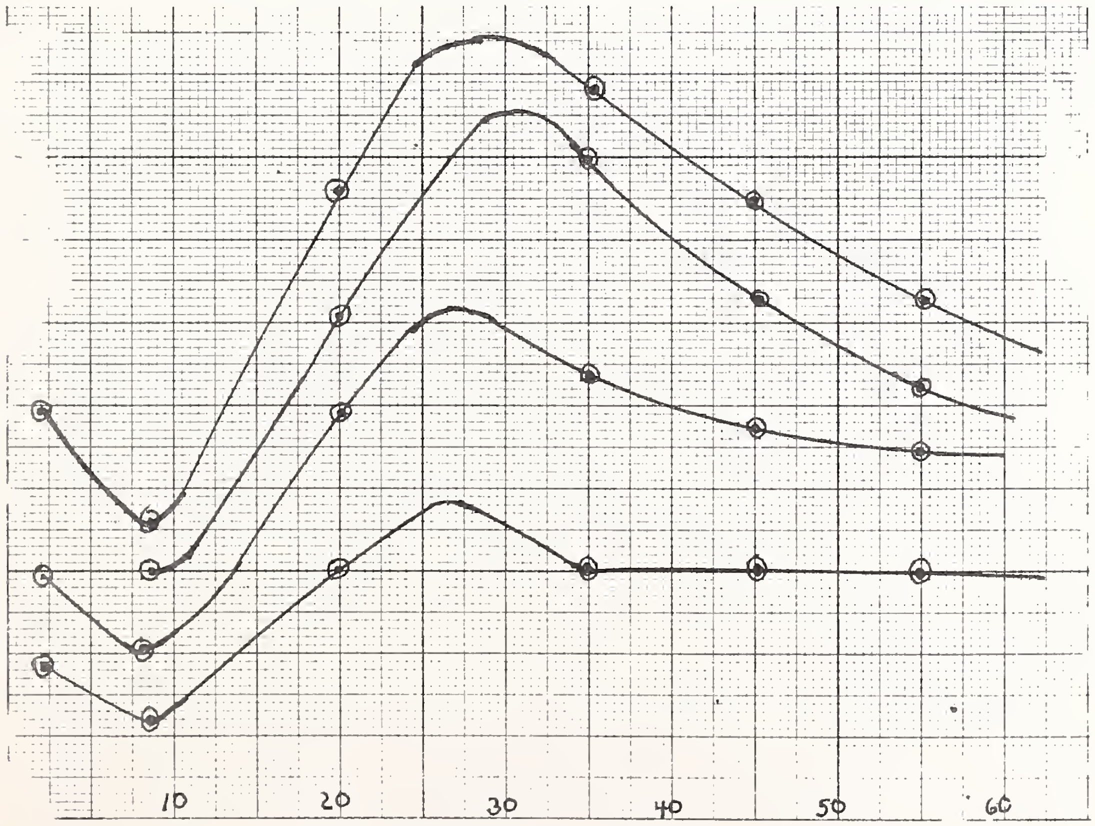


PLATE 6

Activation Energy

Several attempts were made to obtain adsorption data at different temperatures but these met with little success due to poor temperature control. The relaxation times are very short and the temperature susceptability is small and this limits the design of suitable experiments. A more accurate means of monitoring concentration is required than the polarograph. The slopes of the isotherms are undoubtedly related to the activation energy, but there is no suitable mathematical model available for adsorptions from solution at the present time.

POLAROGRAPHIC TECHNIQUES

Calomel Half-Cell Preparation

The agar gel is prepared by adding 100 ml. of cold water to 3 to 3.5 g. of granulated or finely cut agar. The mixture is heated on the steam bath (heating with a flame causes scorching) and shaken or stirred until a homogeneous solution is obtained. Then 25 g. of solid potassium chloride is added and the solution is stirred until the salt dissolves.

The agar gel, heated to fluidity on the steam bath, is blown into the side arm of the cell. The side arm is filled completely with the molten agar, and is held in a vertical position until the gel solidifies. When a saturated calomel reference anode is used the agar gel is saturated with potassium chloride. If it is necessary to avoid chloride ion a mercury-mercurous sulfate reference anode in saturated potassium sulfate may be used, in which case the agar gel is prepared with about 1 M potassium nitrate (the agar does not solidify satisfactorily if potassium sulfate is used).

Supporting Electrolyte

Concentration for the majority of the tests used a .1M KCL solution as a supporting electrolyte. This electrolyte has been used extensively due

to its neutral properties and to the fact that the ion mobility is high in this medium. It also allows a broader use of voltage tolerance because the transference of Potassium ions does not occur until approximately -2.17 V. vs. S.C.E.

TABLE II

POLAROGRAPHIC DATA
DECOMPOSED GRANITE

Mesh Size	Standard Concentration	Sample Concentration	Diffusion Current	Relative Adsorption
+8	.001	-	2.43	
"	-	.000775	1.88	.55
"	.003	-	7.13	-
"	-	.00267	6.32	.81
"	.007	-	17.7	-
"	-	.0065	16.2	1.50
8-10	.001	-	2.62	-
"	-	.00088	2.34	.29
"	.003	-	7.98	-
"	-	.00282	7.70	.28
"	.005	-	13.49	-
"	-	.00476	12.85	.64
"	.007	-	19.47	-
"	-	.00660	18.40	1.07
10-30	.001	-	2.82	-
"	-	.000741	2.09	.73
"	.003	-	8.06	-
"	-	.00254	6.82	1.24
"	.005	-	13.92	-
"	-	.00442	12.30	1.67
"	.007	-	19.93	-
30-40	-	.00637	18.06	1.87
"	.001	-	2.69	-
"	-	.00716	1.87	.82
"	.003	-	8.10	-
"	-	.00253	6.78	1.40
"	.005	-	13.76	-
"	-	.00426	11.85	1.91
"	.007	-	19.3	-
"	-	.0062	17.1	2.20
40-50	.001	-	2.20	-
"	-	.000664	1.46	.74
"	.003	-	7.20	-
"	-	.0025	6.00	1.20
"	.005	-	12.82	-
"	-	.0044	11.28	1.54
"	.007	-	18.00	-
"	-	.00626	16.30	1.70
50-60	.001	-	2.41	-
"	-	.000625	1.51	.90
"	.003	-	7.50	-
"	-	.00254	6.48	1.02
"	.005	-	12.45	-
"	-	.00444	11.12	1.33
"	.007	-	17.35	-
"	-	.00635	15.75	1.60

TABLE II
(Cont.)

60-80	.001	-	2.47	-
"	-	.00053	1.31	1.16
"	.003	-	7.45	-
"	-	.0026	6.44	1.01
"	.005	-	12.61	-
"	-	.00456	11.47	1.14
"	.007	-	17.27	-
"	-	.0006	16.28	.99
80-100	.001	-	2.13	-
"	-	.000619	1.30	.80
"	.003	-	7.33	-
"	-	.00246	6.00	1.33
"	.005	-	12.87	-
"	-	.00434	11.20	1.67
"	.007	-	17.9	-
"	-	.00621	15.9	2.0
100-200	.001	-	2.33	-
"	-	.000592	1.38	.95
"	.003	-	7.11	-
"	-	.00199	4.71	2.40
"	.005	-	11.72	-
"	-	.0041	9.60	2.12
"	.007	-	17.3	-
"	-	.00615	15.2	2.1
-200	.001	-	2.25	-
"	-	.000360	.81	1.44
"	.003	-	7.27	-
"	-	.00176	4.26	3.01
"	.005	-	12.03	-
"	-	.00336	8.08	3.95
"	.007	-	17.8	-
"	-	.0052	13.2	4.6
Total	.0001	-	3.60	-
"	-	.000095	.342	.18
"	.0003	-	.757	-
"	-	.000127	.320	.437
"	.0005	-	1.31	-
"	-	.000222	.58	.73
"	.0007	-	1.70	-
"	-	.00041	.99	.71
"	.001	-	2.29	-
"	-	.0007	1.60	.69
"	.003	-	6.88	-
"	-	.00246	5.65	1.23
"	.005	-	11.31	-
"	-	.00448	10.13	1.18
"	.007	-	16.0	-
"	-	.00635	14.5	1.5

TABLE III

POLAROGRAPHIC DATA
CRUSHED GRANITE 8-10 MESH

Standard Concentration	Sample Concentration	Diffusion Current	Relative Adsorption
.001	-	2.70	-
-	.00086	2.32	.38
.002	-	5.21	-
-	.00188	4.90	.31
.003	-	7.80	-
-	.00280	7.26	.54
.005	-	13.32	-
-	.0046	12.24	1.08
.007	-	19.0	-
-	.00637	17.3	1.70

TABLE IV

POLAROGRAPHIC DATA
OTTAWA SAND

Mesh Size	Standard Concentration	Diffusion Current	Relative Adsorption
30-40	.001	2.34	--
	-	2.32	.02
	.003	6.77	--
	-	6.77	.00
	.005	11.68	--
	-	11.36	.32
	.007	16.43	--
	-	15.98	.45
40-50	.001	2.43	--
	-	2.28	.15
	.003	7.36	--
	-	7.16	.20
	.005	11.63	--
	-	11.52	.11
	.007	17.3	--
	-	16.4	.9
50-60	.001	2.58	--
	-	2.35	.23
	.003	7.12	--
	-	6.84	.28
	.005	11.39	--
	-	11.09	.30
	.007	16.7	--
	-	15.7	1.0
60-80	.001	2.88	--
	-	2.65	.23
	.003	7.25	--
	-	6.71	.54
	.005	11.84	--
	-	11.44	.40
	.007	17.0	--
	-	16.3	.7
80-100	.001	2.67	--
	-	2.62	.05
	.003	7.40	--
	-	7.36	.04
	.005	12.70	--
	-	12.23	.47
	.007	17.70	--
	-	17.16	.54

TABLE IV
(continued)

100-200	.001	-	2.62	2.64	2.64	2.63	-	25.0
	-	.001	2.57	2.52	2.56	2.55	.08	25.0
	.003	-	8.00	8.00	8.08	8.02	-	25.0
	-	.003	7.88	7.88	7.94	7.90	.12	25.0
	.005	-	13.28	13.20	13.20	13.23	-	27.0
	-	.005	12.88	12.80	12.80	12.83	.40	26.5
	.007	-	19.15	18.85	18.80	18.90	-	25.5
	-	.007	17.75	17.80	17.85	17.80	1.10	25.0
-200	.001	-	2.62	2.52	2.48	2.54	-	24.0
	-	.001	2.06	2.04	2.00	2.03	.51	23.5
	.003	-	7.76	7.72	7.76	7.25	-	25.0
	-	.003	7.12	7.20	7.20	7.17	.58	25.0
	.005	-	12.72	12.60	12.64	12.65	-	24.0
	-	.005	11.84	11.92	11.92	11.89	.76	24.0
	.007	-	17.8	17.7	17.8	17.76	-	24.0
	-	.007	17.7	17.5	17.4	17.53	.23	24.0
28-200	.001	-	2.37	2.37	2.34	2.36	-	22.0
	-	.001	2.35	2.31	2.30	2.30	.06	22.0
	.003	-	7.16	7.08	7.00	7.12	-	23.0
	-	.003	6.84	6.80	6.84	6.83	.29	23.5
	.005	-	11.84	11.76	11.84	11.81	-	24.0
	-	.005	11.60	11.52	11.52	11.55	.26	24.0
	.007	-	16.60	16.60	16.60	16.60	-	21.5
	-	.007	16.30	16.30	16.30	16.30	.30	24.0

TABLE V

POLAROGRAPHIC DATA
LIMESTONE
$ZnSO_4$ SOLUTION

Standard Concentration	Sample Concentration	Diffusion Current	Relative Adsorption
.001	-	2.63	-
-	.00019	.50	2.13
.003	-	8.11	-
-	.00067	1.81	6.30
.005	-	13.2	-
-	.00123	3.22	10.00
.007	-	18.50	-
-	.00284	5.22	13.2

$ZnCl_2$ SOLUTION

Standard Concentration	Sample Concentration	Diffusion Current	Relative Adsorption
.001	-	2.23	-
-	.000139	.31	1.92
.002	-	4.24	-
-	.000284	.40	3.84
.003	-	6.75	-
-	.000466	1.01	5.74
.005	-	10.98	-
-	.000852	1.94	9.04
.007	-	15.75	-
-	.00174	3.90	11.85

TABLE VI

POLAROGRAPHIC DATA
BASIC SLAG
$ZnSO_4$ SOLUTION

Standard Concentration	Diffusion Current	Relative Adsorption
.001	2.38	-
-	2.14	.19
.002	4.52	-
-	4.08	.37
.003	6.66	-
-	6.12	.54

$ZnCl_2$ SOLUTION

.001	2.32	-
-	1.95	.37
.002	4.57	-
-	3.64	.93
.003	6.58	-
-	5.28	1.30
.005	11.41	-
-	9.46	1.95
.007	15.80	-
-	13.23	2.60

TABLE VII

POLAROGRAPHIC DATA
ANDESITE
$ZnSO_4$ SOLUTION

Standard Concentration	Diffusion Current	Relative Adsorption
.001	2.85	-
-	2.66	.19
.002	5.73	-
-	5.44	.29
.003	8.60	-
-	8.18	.42
.005	13.89	-
-	13.44	.45
.007	20.1	-
-	19.4	.70

PART III

AGGREGATE ASPHALT INTERACTIONS

The Strip Test

The only means currently available for evaluating the behavior of different aggregates with respect to asphalt adhesion is the strip test. The following are standards in procedure and evaluation.

(1) Blending of heated asphalt with aggregate; four hours cooling time; twenty-four hours under water; five minutes in a Red-Devil paint shaker; removal for evaluation.

(2) Use of a standard asphalt (Farmers MC-5).

(3) At least three tests for each type of aggregate are performed and the average is determined.

(4) Adhesion is evaluated by three different observers. (The individual evaluations should not vary more than $\pm$ 5% for any sample or group of identical samples).

(5) A petrographic analysis of each sample is obtained.

The test is by nature a comparison test. Its long term validity depends on using the same standard asphalt, on shaker design, and on individual evaluating skill. Nevertheless, it has proven reproducable to within 5%. For more complete details, see the appendix of this section.

The main source of error involved is the degree of wear that a given aggregate may undergo. Hard and soft materials may behave differently under the test. It is also important that asphalt characteristics be kept constant. Continual heating of asphalt causes loss of volatiles which changes the characteristics. Different parts of the shaker produce different amounts of agitation so samples to be compared must be placed in the same location

in the shaker.

The strip test has proven very useful in evaluating adhesive agents, as these can be added to standard asphalts and used with standard or representative aggregates. This has been the procedure used to determine acceptable adhesive agents.

<u>Experimental Study</u>

The aggregates used in the adsorption experiments were evaluated by means of the strip test with the standard asphalt (Farmers MC-5). As indicated in Part I, any Lewis base stronger than water should behave as an adhesive agent. The use of amines for this purpose has been indicated. As a second choice we have picked stearic acid. Organic acids behave as Lewis Bases since the carbonyl group is electron rich and can share electron pairs. The organic acids are weaker Lewis Bases than amines, so their effects as an adhesive agent should be less. Strip tests were performed for six aggregate types using:

(a) No surface active agent, (b) Acra as the amine adhesive agent, and

(c) Stearic acid as an adhesive agent.

The combining of stearic acid with asphalt was readily achieved. The wax-like appearing acid dispersed readily in the asphalt and required little mixing. No odor is detected for stearic acid as in the Acra samples. Aggregate with an asphalt-stearic acid coating has a different luster from the glossy black coating containing Acra. It appears more as a metallic or crystalline luster. The stearic acid used in the testing was obtained from Emery, Fatty Acid Division, as Hyfac 400 Hydrogenated Fatty Acid (65% stearic acid, 35% palmitic acid).

Petrographic Data

Lab. #227257--Test #1616

Quartzite - 40%

Argillaceous Quartzite - 20%

Argillite - 30%

Greywacke Sandstone - 10%

Quartzite - metamorphosed sandstone cemented with silica, much free SiO_2.

Argillite - metamorphous rock; hard and massive clay stone (hydrous aluminum silicate with Ca, K, etc.), less free SiO_2.

Greywacke sandstone - very fine particles of quartz held in a matrix of fine materials, water worn.

In general, the surface reactivity of this aggregate sample might be represented in two groups:

(1) Quartzite and Argillaceous quartzite

High SiO_2 content 65-80%

(2) Argillite and Greywacke Sandstone

Smaller SiO_2 content. There is a decrease in quartz and an increase in ferro-magnesium minerals and some feldspar.

Lab. #226542--Test #1601

Limestone - 90%

Quartzite - 10%

Limestone - calcite is the chief constituent of limestone.

The sample was compact and coarse.

Quartzite - excess SiO_2.

Lab. # 227516--Test #1640

Granite, Porphyritic Granite, Granite Gneiss - 60%

Quartzite - 20%

Shale - 10%

Hornfels - 10%

Granite, Porphyritic Granite, Granite Gneiss: Contains a high percentage of SiO_2, 65 to 80%, some feldspar and a smaller amount of ferromagnesium minerals.

Shale: Clay, quartz and feldspar occurring as a very fine and evenly grained rock. These fine particles have been mechanically carried by the water and the surface chemistry has been altered as a result of the action with the soluble salts in water.

Hornfels: Highly metamorphosed silicate rock. The small particles of this sample have been steam and gas altered. Like shale, the surface is quite inert.

Lab. # 227840--Test #1672

Vesicular and Glassy Basic Slag - 100%

Vesicular and Glassy Basic Slag:

No free SiO_2. High proportion of ferromagnesium silicate and metallic ions. Structurally unstable, basic slag is highly reactive, particularly with an acid.

Lab. # 222392--Test #1378

Andesite - 100%

Andesite: The SiO_2 content, between 65 and 52 percent of andesite classifies it as intermediate, as opposed to acidic or basic. A sodium plagioclase containing hornbelnde, augite, hypersthene, or biotite.

Lab. # 222392--Test #1378 (Cont.)

This sample contains a considerable quantity of Ca, Mg, Fe, Al, and K.

Lab. # 228305

Sandstone - 100%

Sandstone: A water-worn feldspathic quartzite; consolidated quartz grains cemented together with feldspar. The chemical composition of feldspar is M $AlSi_3O_8$ or M' $Al_2Si_2O_8$ in which the metal may be potassium, sodium, or calcium. The cementing material has less free SiO_2.

Conclusions:

Stearic Acid as a Surface Active Agent

In the classification of rocks according to chemical composition, they are referred to as acid, intermediate, or basic, dependent in general upon quantity and combinations of free SiO_2, ferro-magnesium minerals, feldspar, olivine, and other minerals. Their theoretical ability, based on probable chemical reaction, for surface reaction with Lewis Bases such as Amines or Stearic Acid might be categorized as follows:

Highly altered, weathered rock; shale, hornels, etc.	- 0%
Quartzite, granite, sandstone, etc.	-50%
Quartzite with moderate feldspar; argillite, etc.	-75%
Intermediate; andesite, diorite, etc.	-100%
Basic Slag, basalt	-100%

We note the conflict of terminology. As we proceed down the list, the Lewis acidity increases. The latter members are designated basic, however, by the geologists since they react with the mineral acids. Our terminology reflects the relative ability of receiving an electron pair from asphalt,

water, etc. to form a chemical bond and is a much broader designation. This classification is in agreement with the adsorption studies. In solution or in a static state, the stronger Lewis acids such as basalt should acquire a negative charge as they satisfy their quest for electrons, or should at least be negative with respect to those above them in the list.

Experimental results are in agreement with these values for the evaluated samples. In all cases, with the exception of the sandstone sample, adhesion with stearic acid-asphalt equalled or exceeded that with Acra. Acra, being a basic surface active agent, would exhibit greater adhesion than stearic acid with rocks whose basisity exceeds that of stearic acid (as a Lewis Base).

One can also conclude from the samples tested with plain Farmers' MC-5 asphalt, that the asphalt itself was of a mildly Basic nature contributing to the greater adhesion with the aggregates limestone and slag.

The strip test data is given in Table I. This should be compared to the adsorption data of Plate 3 of Part II. There is almost a linear relation between the percent adhesion and the relative adsorption. The single exception to this is in the case of the basic slag. The surface of this material is highly covered with anions and perhaps adsorbed water as evidenced by the shift in the adsorption curves for the sulfate and chloride and so the isotherm or its intercept may not be a good indication of its true adsorptive powers.

The high effectiveness of the stearic acid is difficult to account for on the basis of its strength as a Lewis base. Several other organic acids were also checked as adhesive agents. A high molecular weight seems to be necessary. In particular itaconic acid and some of its derivitives (dibutyl and di methyl itaconate) were checked and found to increase adhesion by about 5 to 10 percent. These particular compounds are crosslinking agents in plastic but they showed no similar tendency with the asphalt.

The polar character of asphalt may be controlled or altered by the addition of a long-chain organic molecule containing a polar end. Stearic acid is such a molecule.

$$\underset{\text{Non-Polar}}{CH_3}\ (CH_2)_{16}\text{-}\underset{\substack{\text{Polar}\\ \text{(Anionic)}}}{C\text{-}OH}$$

The non-polar portion of the molecule is soluble in asphalt, whereas the polar end will orientate itself toward an opposite polar group such as exists on electropositive aggregate surfaces.

$$Agg\text{-}Ca\text{-}CO_3H \xrightarrow{\substack{\text{in acid}\\ \text{medium}}} Agg\text{-}Ca^+ \xrightarrow{\substack{\text{with stearic}\\ \text{acid}}} \underset{\substack{\text{soluble in}\\ \text{asphalt}}}{Agg\text{-}Ca\text{-}O\text{-}C\ (CH_2)_{16}CH_3}$$

As illustrated, the stearic acid acts as the link between the aggregate surface and asphalt.

The difficulty with this hypothesis, however, is the fact that the stearic acid must be at the interface in order to be effective. Initially, there is a uniform distribution of the agent throughout the asphalt. In order to be effective as a coupling agent, the acid must accumulate at the interface. Free translation of a large molecule through the viscous asphalt is an extremely slow process, if it occurs at all, so the surface concentration cannot exceed 0.5% by any great degree. The difference in bonding strength between the rock and the acid and the rock and the normal asphaltic components cannot differ by more than a factor of ten at the most. We should then expect the bonding to be increased by 5% or less in all cases.

There is, of course, no reason why all adhesive agents should work in the same way. The coupling mechanism may be possible if the asphalt were heated to a high enough temperature so that an appreciable concentration of the agent could accumulate at the stone interface. The performance of this agent should then be very dependent on mixing temperature and grade of asphalt.

TABLE I

SAMPLE	QUARTZITE	LIMESTONE	GRANITE	SLAG	ANDESITE	SANDSTONE
	227257	226542	227516	227840	222392	228305
(1) MC-5 Asphalt	10% Adhesion	35-40% Adhesion	25% Adhesion	90% Adhesion	15% Adhesion	25% Adhesion
(2) MC-5 Asphalt +½% Stearic Acid	50% Adhesion	55-60% Adhesion	45% Adhesion	100% Adhesion	90% Adhesion	35% Adhesion
(3) MC-5 Asphalt +1% Stearic Acid	65-70% Adhesion	60-65% Adhesion	55% Adhesion	100% Adhesion	100% Adhesion	40% Adhesion
(4) MC-5 Asphalt 1/2% Acra	30% Adhesion	40% Adhesion	35% Adhesion	90% Adhesion	100% Adhesion	85% Adhesion
(5) MC-5 Asphalt 3/4% Acra	45% Adhesion	50% Adhesion	35% Adhesion	95% Adhesion	100% Adhesion	95% Adhesion

The alternative explanation is to assume that the agent prevents the accumulation of water at the mineral interface. The presence of a monolayer of adsorbed oxygen on the stone prior to mixing, or of water of hydration for that matter could alter the picture considerably.

pH and Surface Reactivity - Emulsions

The following tables have been compiled to demonstrate the reactivity of aggregate types as corresponding to the pH and available surface active agents of the bituminous material. Comparative adhesion was demonstrated for all but acid-anionic medium; chemical reaction occurs with acid and an anionic agent producing an inert precipitate.

Table II illustrates the behavior of Lewis Acidic type aggregate. The surface reactivity will be most like that of limestone. Such surfaces in solution tend to be coated with electron rich, or negatively charged atoms. The presence of acid reduces the number of these and so increases the odds of bonding with the asphalt.

Table III illustrates the behavior of acid-type aggregate. The surface reactivity of these samples is expected to follow most closely that of quartzite. Such surfaces in solution tend to be coated with electron deficient or positively charged atoms. A decrease in the number of these increases the odds of bonding with the asphalt.

TABLE II

INTERMEDIATE TO BASIC AGGREGATE

AGGREGATE SAMPLES	ACID CATIONIC	BASIC CATIONIC	BASIC ANIONIC
10% Quartzite 10% Lime 65% Intermediate to basic	80% Adhesion	50% Adhesion	Very poor adhesion
60% Intermediate 15% Basic	70% Adhesion	40% Adhesion	Very poor adhesion
80% Intermediate 10% Basic 10% Acid	70% Adhesion	10% Adhesion	Very poor adhesion
25% Acid 75% Intermediate	50% Adhesion	30% Adhesion	Very poor adhesion
35% Acid 55% Intermediate 10% Basic	20% Adhesion	20% Adhesion	Very poor adhesion

TABLE III

AGGREGATE SAMPLES	ACID CATIONIC	BASIC CATIONIC	BASIC ANIONIC
85% Quartzite - Argillite	87% Adhesion	94% Adhesion	Poor to very poor adhesion
50% Quartzite - Argillite 15% Granite	91% Adhesion	98% Adhesion	Poor to very poor adhesion
50% Quartzite - Argillite 15% Granite	85% Adhesion	95% Adhesion	Poor to very poor adhesion
25% Quartzite 50% Granite	20% Adhesion	75% Adhesion	Poor to very poor adhesion
50% Quartzite 10% Granite 10% Argillite	85% Adhesion	95% Adhesion	Poor to very poor adhesion
35% Quartz-Quartzite 35% Granite 5% Argillite	20% Adhesion	70% Adhesion	Poor to very poor adhesion
70% Quartzite 10% Granite	50% Adhesion	95% Adhesion	Poor to very poor adhesion
30% Argillite 50% Quartzite 5% Granite	40% Adhesion	98% Adhesion	Poor to very poor adhesion

Strip Test

Aggregate of size -3/4 + 4M is tested with untreated and treated asphalt cement, -5/8 + 8 and 3/8 cover with untreated and treated MC-5, while -3/8 + 8M material is used with Cationic and Anionic Emulsions.

Approximately 200 grams are weighed and placed in an oven at 250° F. along with the asphalt to be used. Both are heated until the asphalt can be readily poured.

The aggregate is mixed on a hot-plate with just enough asphalt to thoroughly coat the aggregate surfaces. A metal pan and putty knife are used to accomplish the mixing. The mixture is left to cure in the air until it is cold to the touch. Asphalt cement is used with plant-mix aggregate; MC-5 is used with road mix and seal-coat aggregate.

The procedure for emulsions varies slightly. To 150 grams of the aggregate are added 50 grams of emulsion, and the mixture is stirred until all of the aggregate is covered. Excess emulsion is drained off on an elevated 4M wire screen, and the mixture is cured overnight at room temperature.

After the aggregates for both the asphalt cement, cutbacks, and emulsion adhesion tests have been sufficiently cured in air (aggregate tested with an asphalt cement, or cutbacks, are removed from the mixing pans with a putty knife after the pans have first been heated on a hot plate for about 3 seconds), they are immersed in a quart jar containing one (1) pint of water at ± 7.8 pH and at 70° F. temperature. The mixture remains thus for twenty-four (24) hours.

At the end of the soaking period, the mixture is transferred to a half-gallon friction-lid, metal can and a second pint of water is added.

The mixture is shaken in a "Red Devil" paint shaker for four (4) minutes. The aggregate and asphalt mixture is then carefully washed to remove any loose asphaltic material and spread on a paper towel. Evaluation of adhesion is made only when the aggregate is thoroughly dry. A visual estimate of the proportion of the surfaces remaining coated with asphalt is made and the results are expressed and reported as % adhesion.

Adhesive Agent Specifications

The following is a set of Specifications for adhesive agents based on the work with the strip test.

Any adhesive agent to be contained in asphalt must meet the following specifications:

(1) Be heat stable at all temperatures to which the asphalt may be subjected during normal maintenance procedures.

(2) Be injected and homogeneously mixed in the asphalt bulk at a minimum concentration of 1/2% by volume upon delivery.

(3) Provide satisfactory adhesion at 1/2% concentration by volume in asphalt. That is, provide adhesion within 10% of that achieved by a standard adhesive agent. This determination is met in simultaneous testing for five sets of aggregate samples using both the standard adhesive agent and the adhesive agent under consideration according to strip test procedures as outlined by the Montana State Highway Commission Laboratory.

(4) Upon heating, the asphalt-adhesive agent mixture should not dispel an odor too objectionable for working conditions.

The following commercial adhesive agents have been investigated during the course of this study:

Redicote 80-S

Acra 300 - slight objectionable odor

Phillips Additive

Arosurf AA-32*

Arosurf AA-11

*Recommended for refinery mixing only.

The foregoing have been used now by the Montana Highway Commission for about 18 months.

Field Observations on Adhesive Agents

The following are some of the observations made in the Field by maintenance personnel in the use of adhesive agent with asphalt. Also indicated are some recommendations for improvement of use.

OBSERVATIONS	RECOMMENDATIONS
1. Some loss in workability of asphalt, particularly observed for winter stockpiles. (Butte and Billings)	1. Use of a less viscous asphalt should alleviate this effect. That is, use of an MC-250 with adhesive agent in place of MC-800 especially for winter stockpiles.
2. "Drying up" of stockpiles stored over winter. (Helena)	2. This is probably an effect of increased viscosity rather than "drying up". Summer temperatures should restore the softness. Again, this may be prevented by use of a lighter asphalt.
3. Ease of blading stockpiles due to uniformity of mixture even after winter storage.	3. None. The increased adhesive quality is expected to prevent "leaching" of asphalt and separation of aggregate from asphalt.
4. Loss in gloss of asphalt.	4. This is probably a physical change, and should have no effect on asphalt behavior.
5. Non-workable for cold patches.	5. The increased cohesiveness or "stickiness" of asphalt probably renders such a mix non-usable for cold patching unless a lighter asphalt is used or cold patching is done during hot weather.

In general, it is known that asphalt with adhesive agent does, somewhat, increase in viscosity. The material also becomes more susceptible to temperature; however there is no loss in its elastic properties. It is because of these properties that the mix is less susceptible to water and "stripping" is prevented or limited.